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SHORT COMMUNICATION

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Production of micron-sized, monodispersed, multihollow polystyrene/poly(3,5-xylidine) composite particles by chemical oxidative seeded polymerization

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Abstract Micron-sized, monodispersed polystyrene/poly(3,5-xylidine) composite polymer particles were produced by chemical oxidative seeded polymerization of 3,5-xylidine with 1.37-μm-sized, monodispersed polystyrene seed particles. The chemical oxidative seeded polymerization was conducted in an aqueous medium at 25 °C in the presence of poly(vinyl alcohol) as a stabilizer using ammonium persulfate as an oxidant. The composite particles had a multihollow structure.

Key words 3,5-Xylidine · Chemical oxidative polymerization · Micron size · Monodisperse · Multihollow

Introduction

Polymer particles produced by emulsion polymerization of vinyl monomers have been widely used in industrial applications, for example, adhesives, inks, and coatings. Recent applications include their use in the colloidal state as carriers for chromatography and as immobilizers of biomolecules because of their large specific surface area and the easy control of their surface characteristics. In addition to these functional polymer particles produced by heterogeneous polymerization of vinyl monomers, the chemical oxidative polymerization of nonvinyl monomers, such as pyrrole and aniline, has been studied in recent years [1–9].

Armes et al. [1] reported that sub-micron-sized polypyrrole particles were produced by chemical oxidative polymerization in an aqueous medium in the presence of iron(III) chloride as an oxidant and that a pellet of the particles had electrical conductivity. Abe et al. [2] showed that the chemical oxidative polymerization of aniline in HCl aqueous solution was possible with ammonium persulfate (APS) as an oxidant. Spherical and needle-shaped, sub-micron-sized polyaniline particles were produced using various stabilizers by Vincent and Waterson [3]. Snauwaert et al. [10] carried out polymerizations of dimethylanilines using APS or potassium dichromate as an oxidant and pointed out that 3,5-xylidine (Xy) did not give polymeric products. Toshima and Yan [11] also reported that no polymeric products were obtained from Xy with APS. However, we succeeded in producing poly(3,5-xylidine) (PXy) particles by chemical oxidative dispersion polymerization of Xy with APS in an aqueous medium [12]; the particles had spherical and needle-like shapes and were "polydisperse". In a recent paper, we reported the synthesis of 1.85-μm-sized, "monodispersed" polystyrene (PS)/(PXy) core/shell composite particles by chemical oxidative seeded dispersion polymerization of Xy with PS seed particles [13]. In the polymerization system, almost all of the Xy and APS exist in the aqueous medium. Micron-sized, "monodispersed" polymer particles have been applied in the biomedical field, microelectronics, and other fields.

Recently, in addition to seeded dispersion polymerization, we succeeded in producing micron-sized, "monodispersed" composite polymer particles by seeded polymerization of vinyl monomers, such as divinylbenzene [14] and ethyl methacrylate [15], for the dispersion of highly monomer particles prepared by the dynamic swelling method. In this polymerization system, almost all the monomers and initiators existed in the swollen particles. We have discussed the difference in morphologies produced by the seeded dispersion polymerization and the seeded polymerization for swollen particles [16].

Here, we report the production of micron-sized, monodispersed, "multihollow" PS/PXy composite particles by chemical oxidative seeded polymerization of Xy with 1.37-μm-sized, monodispersed PS particles in a heterogeneous medium.

Experimental

Materials

Guaranteed grade Xy, APS, 1,4-dioxane, and extra reagent grade ethanol and ethylene glycol were used as received from Nacalai Tesque Co. Deionized water with a specific conductivity of 5×10^6 Ω cm was distilled once using a Pyrex distillator. Poly(vinyl alcohol) (PVA) was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification: 88%). Styrene and acrylic acid (AA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Extra reagent grade 2,2′-azobis(isobutyronitrile) was purified by recrystallization. Poly(acrylic acid), used as a stabilizer, was produced by solution polymerization of AA in 1,4-dioxane, according to the method described in a previous article [17].

Preparation of seed particles

Micron-sized, monodispersed PS seed particles were produced by dispersion polymerization at 70 °C for 24 h with an anchor-type stirrer at 60 rpm under a nitrogen atmosphere in a four-necked round-bottomed flask under the optimum conditions listed in Table 1, as reported in a previous article [17].

Swelling of seed particles with Xy

Swelling of the PS particles with Xy was carried out at 25 °C for 12 h under the conditions listed in Table 2 as follows. Water (36 g), Xy (1 g), and PVA (0.5 g) were charged into a glass cylindrical reactor and the PS particles (1 g) were dispersed in this mixture. The reaction mixture in the flask was stirred with a magnetic stirrer at 300 rpm. It was confirmed experimentally using gas chromatography that 80% of the Xy monomers were absorbed by the PS seed particles before polymerization.

Chemical oxidative seeded polymerization

Chemical oxidative seeded polymerization for the dispersion of Xy-swollen PS particles was carried out in a glass cylindrical reactor under a nitrogen atmosphere at 25 °C for 8 days as follows. To the dispersions of Xy-swollen PS particles, three portions of APS (1.88 g) aqueous solution (5 g) were added stepwise at 24-h intervals. The PS/PXy composite particles obtained were washed repeatedly by centrifugation before further experiment.

The particles were observed using a Nikon MICROPHOT-FXA optical microscope, a JEOL JEM-2010 transmission electron microscope (TEM), and a Hitachi S-2500 scanning electron microscope (SEM).

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

Ingredients	Weight (g)
Styrene	100
2,2′-Azobis(isobutyronitrile)	1.68
Poly(acrylic acid)	12
Ethanol	685
Water	200

Measurement of the conversion

The amount of unreacted Xy was measured by gas chromatography (Shimadzu Co., GC-18A) with helium as a carrier gas. Ethylene glycol and 1,4-dioxane were used as a standard reagent and as a solvent, respectively. The temperature of the measurement were 300 °C for the injector and the detector and 220 °C for the column.

Particle size distribution

The number-average diameter (D_n) and the coefficient of variation (C_v) were measured from TEM photographs using the Mac Scope program (MITANI Co.).

Observations of the ultrathin cross sections of particles

A small amount of PS/PXy was added to 20 wt% gelatin aqueous solution, and the mixture was frozen in a refrigerator for 24 h. The ultrathin cross sections with a thickness of about 80 nm were obtained by sectioning at −100 °C with a microtome equipped with a cryopump (Leica, REIHERT FC S, Austria), and they were then transferred to TEM grids treated hydrophilization and observed with a TEM.

Fourier transform IR measurement

The compositions of the composite particles were measured with a Fourier transform (FT)-IR spectrometer (JASCO Co., FT/IR-615R) using a pressed-KBr-pellet technique.

Results and discussion

A TEM photograph of the PS seed particles produced by dispersion polymerization under the condition listed

Table 2 A recipe for the production of PS/poly(3,5-xylidine) composite particles by chemical oxidative seeded polymerization (25 °C; 8 days; stirring rate, 300 rpm) for 3,5-xylidine-swollen PS particles prepared using a conventional swelling procedure. The swelling was carried out at 25 °C for 12 h before the addition of ammonium persulfate (APS)

Ingredients	Weight (g)			
PS seed particles[a]	1.0			
Xylidine	1.0			
APS		1.88[b]	1.88[b]	1.88[b]
Poly(vinyl alcohol)	0.5			
Water	36	5[b]	5[b]	5[b]

[a] Three portions of water (5 g) with dissolved APS (1.88 g) were added stepwise at 24-h intervals

[b] D_n = 1.37 μm; C_v = 4.0%

in Table 1 is shown in Fig. 1. The PS seed particles were spherical and monodisperse: D_n and C_v were 1.37 μm and 4.0%, respectively.

Optical photographs of the PS seed particles and the particles swollen with Xy in the absence of APS under the conditions listed in Table 2 are shown in Fig. 2. The swollen particles had high monodispersity and their contrasts were homogenous. Chemical oxidative seeded polymerization of the swollen particles was carried out with APS and resulted in a highly stable emulsion of PS/PXy composite particles. The initial polymerization was very fast and the conversion reached about 64% after 1 h, but the rate gradually became slow. After 24 h the conversion reached about 76% and did not become any higher with one portion of APS aqueous solution. To complete the polymerization, 2 mol APS was added stepwise for each mole of Xy at 24-h intervals. After 8 days the polymerization was almost complete.

Optical, SEM, and TEM photographs of the composite particles produced are shown in Fig. 3: D_n and C_v were 1.72 μm and 3.4%, respectively. The particles obtained were highly stable and a small amount of PXy byproduct was observed with the optical microscope. From the weights of the PS/PXy composite particles and the PXy byproduct particles, collected selectively with a centrifugal procedure, it was determined that 70% of PXy was introduced into the composite particles and that 36% of Xy formed PXy byproduct particles. The total percentage of over 100% may be due to the probable presence of sulfate ions in PXy. In the optical and TEM photographs, the contrast of the inside was heterogeneous. In the SEM photograph, the composite particles had slightly uneven surfaces. The diameter of the particles obtained was more than the 1.60 μm that was calculated assuming that 70% polymerized PXy molecules are included in the PS/PXy composite particles, considering the densities of PS (1.04 [18]) and PXy (1.25 [13]). These results indicate the possibility that the particles obtained had a multihollow structure, and the volume percentage of the hollows was calculated to be 19.4%.

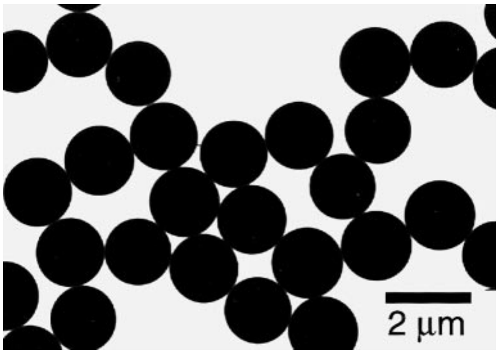


Fig. 1 Transmission electron microscope (*TEM*) photograph of polystyrene (*PS*) seed particles produced by dispersion polymerization under the conditions listed in Table 1

FT-IR spectra of the PS seed particles, PXy, and PS/PXy composite particles are shown in Fig. 4. In the PS spectrum, the characteristic absorption peaks were at 3300–3000 cm^{-1} (aromatic C—H stretching vibration) and at 770–740 and 710–680 cm^{-1} (aromatic C—H out-of-plane bending vibration). In the PXy spectrum, the characteristic absorption peaks were at 3600–3200 cm^{-1} (N—H stretching vibration of an aromatic amine as well as of its salt), 1210–1290 cm^{-1} (C—N stretching vibration), and 1600 cm^{-1} (C=N stretching vibration). Comparing the spectrum of the PS/PXy composite particles with the spectra of the PS and PXy particles, the vibration bands observed for the PS/PXy composite particles can be reasonably assigned to the PS seed particles and PXy. These results indicate that PS/PXy composite particles were successfully produced.

Figure 5 shows TEM photographs before and after the extraction of PS from the PS/PXy composite particles with toluene, which does not dissolve PXy but does dissolve PS, under stirring at room temperature

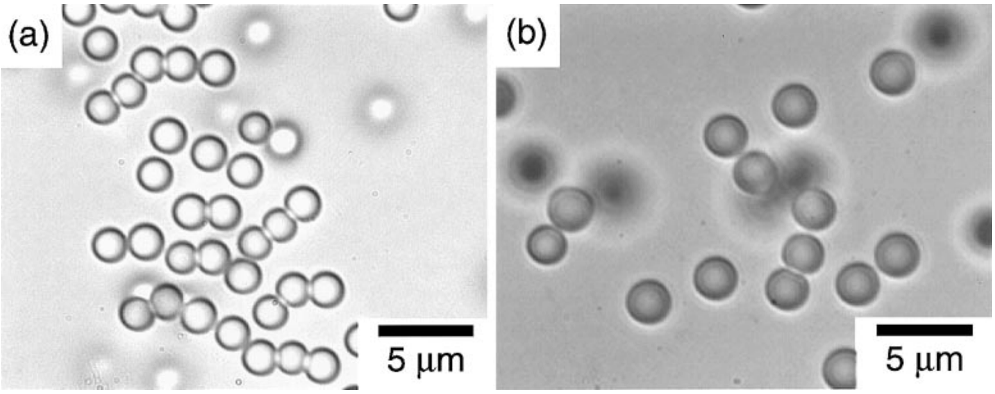


Fig. 2 Optical photographs of **a** PS seed particles and **b** 3,5-xylidine-swollen particles prepared using a conventional swelling procedure under the conditions listed in Table 2

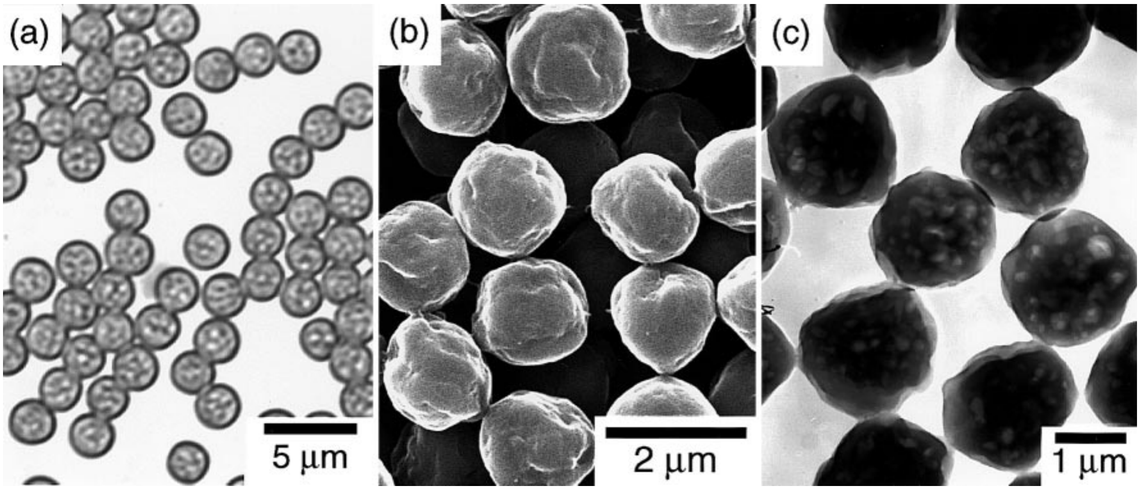


Fig. 3 Optical, scanning electron microscope and TEM photographs of PS poly(3,5-xylidine) (*PXy*) composite particles produced by chemical oxidative seeded polymerization under the conditions listed in Table 2

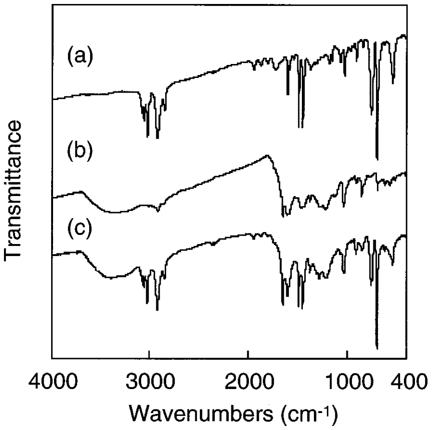


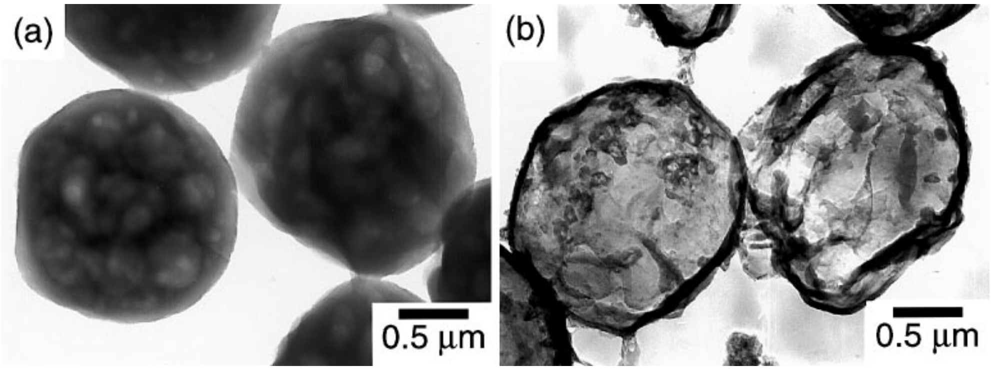
Fig. 4 Fourier transform IR spectra of PS seed particles **a**, PXy particles **b**, and PS/PXy composite particles **c** produced by chemical oxidative seeded polymerization

for 6 days. From a comparison of Fig. 5a and b, the diameter of the PS/PXy composite particles before and after the extraction of PS was almost the same. This indicates PXy formed the shell of the PS/PXy composite particles.

Ultrathin cross sections of the PS seed particles and the PS/PXy composite particles are shown in Fig. 6. The contrast in the PS seed particles is homogeneous, whereas the inside of the composite particles has a multihollow structure; in white regions there is no polymer. Since the polymerization was almost complete, the evaporation of unpolymerized Xy during the drying process is not a reason for the formation of the multihollow structure. This result indicates the possibility that APS aqueous solution diffused into the Xy-swollen PS particles.

A TEM photograph of the ultrathin cross section of the PS/PXy composite particles from which PS was extracted with a few drops of toluene is shown in Fig. 7. From a comparison of Figs. 6b and 7, after the extraction of PS there were high dark regions at the surfaces of the particles and around the hollows. This result suggests that the polymerization proceeds at the internal interfaces formed in the Xy-swollen PS particles

Fig. 5 TEM photographs of PS/PXy composite particles produced by chemical oxidative seeded polymerization **a** before and **b** after the extraction of PS with toluene



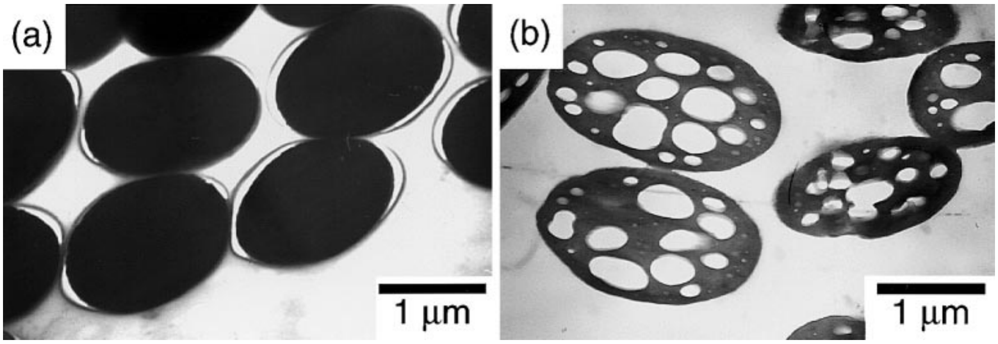


Fig. 6 TEM photographs of ultrathin cross sections of **a** PS seed particles and **b** PS/PXy composite particles produced by chemical oxidative seeded polymerization

and results in multihollow particles with the diffusion of the APS aqueous solution into the inside in addition to that at the external interface.

From these results, it is concluded that micron-sized, monodispersed PS/PXy composite particles having a multihollow structure were produced by chemical oxidative seeded polymerization for the dispersion of Xy-swollen PS particles with APS as an oxidant.

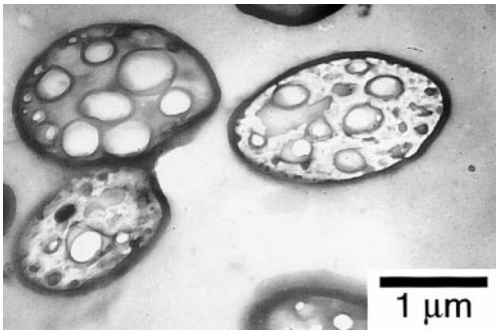


Fig. 7 TEM photograph after the extraction of PS with toluene from ultrathin cross sections of PS/PXy composite particles produced by chemical oxidative seeded polymerization on the TEM grid

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