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SHORT COMMUNICATION

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Production of core/shell polystyrene/poly(3,5-xylidine) composite particles by chemical oxidative seeded dispersion polymerization*

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Abstract Micron-sized monodispersed polystyrene (PS)/poly(3,5-xylidine) (PXy) composite particles were produced by chemical oxidative seeded dispersion polymerization of 3,5-xylidine at 20 °C with 1.6-μm-sized monodispersed PS seed particles in HCl aqueous solution, the pH of which was always kept at 2.5 with a pH stat. The composite particles produced consisted of a PS core and a PXy shell.

Key words 3,5-Xylidine · Chemical oxidative seeded dispersion polymerization · Micron size · Monodisperse · Core/shell morphology

Introduction

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 polypyrrole particles were produced by chemical oxidative polymerization in an aqueous medium in the presence of iron (III) chloride as an oxidant, and 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 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, in a recent communication we reported the synthesis of spherical and needle-shaped poly(3,5-xylidine) (PXy) particles by chemical oxidative dispersion polymerization of Xy with APS in an aqueous medium [12]; the particles were "polydisperse".

Recently, we succeeded in producing micron-sized "monodispersed" composite polymer particles by seeded dispersion polymerization of vinyl monomers such as chloromethyl styrene [13], divinylbenzene [14] and *n*-butyl methacrylate [15] with about 2-μm-sized monodispersed polystyrene (PS) seed particles obtained by dispersion polymerization. Through a series of investigations it was clarified that seeded dispersion polymerization has the advantage that polymer layers accumulate in the order of production, resulting in core/shell particles [16]. Separately, monodispersed PS/polyglutaraldehyde core/shell composite particles having aldehyde groups at their surfaces were produced by aldol condensation seeded dispersion polymerization of glutaraldehyde with 0.5-μm-sized monodispersed PS seed particles in an aqueous medium [17, 18]. Miksa et al. [19] synthesized polypyrrole/polyacrolein core/shell composite particles having aldehyde groups by seeded dispersion polymerization of acrolein with 0.1-μm-sized polypyrrole particles in an aqueous medium.

In this article, we report the production of micron-sized monodispersed PS/PXy core/shell composite particles by the chemical oxidative seeded dispersion polymerization of Xy with PS seed particles.

Experimental

Materials

Analytical grade Xy, HCl, APS and tetrahydrofuran (THF) containing approximately 0.025% butylated hydroxytoluene (BHT) as stabilizer, and reagent grade ethanol were used as received from Nacalai Tesque Co. Deionized water with a specific conductivity of $5 \times 10^6\ \Omega$ cm was distilled once with a Pyrex distillator. Poly(vinyl alcohol) 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. 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 [13].

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-bottom flask under the optimum conditions listed in Table 1, reported in a previous article [13].

Table 1 Preparation of monodispersed polystyrene (*PS*) seed particles by dispersion polymerization[a]

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

[a] N_2; 70 °C; 24 h; stirring rate, 60 rpm

Chemical oxidative seeded dispersion polymerization

Chemical oxidative seeded dispersion polymerizations of Xy were carried out with PS seed particles in HCl aqueous solution at pH 2.5 under the conditions listed in Table 2. It was confirmed experimentally by gas chromatography that almost all the Xy monomer dissolved in HCl aqueous solution before the polymerizations. The pH value was maintained at 2.5 using a pH stat (TOA Electronics, model HSM-10 A) with 1.0 N KOH aqueous solution during polymerization. The PS/PXy composite particles obtained were washed repeatedly by centrifugation before further experiment.

The particles were observed with a Nikon MICROPHOT-FXA optical microscope and a JEOL JEM-2010 transmission electron microscope (TEM).

Table 2 Recipe for the production of PS/Poly(3,5-xylindine) composite particles by chemical oxidative seeded dispersion polymerization of 3,5-xylidine in HCl aqueous medium at pH 2.5[a]

Ingredients				
PS seed particles[b]	(g)	0.75		
3,5-Xylidine	(g)	0.75		
Ammonium persulfate	(g)			2.82[c]
Poly(Vinyl alcohol)	(g)	0.075		
Water	(g)	92.6	+	15[c]

[a] 5, 20 and 35 °C; 48 h; stirring rate, 250 rpm

[b] D_n, 1.56 μm; C_v, 3,8%

[c] 15 g water dissolving 2.82 g ammonium persulfate was added

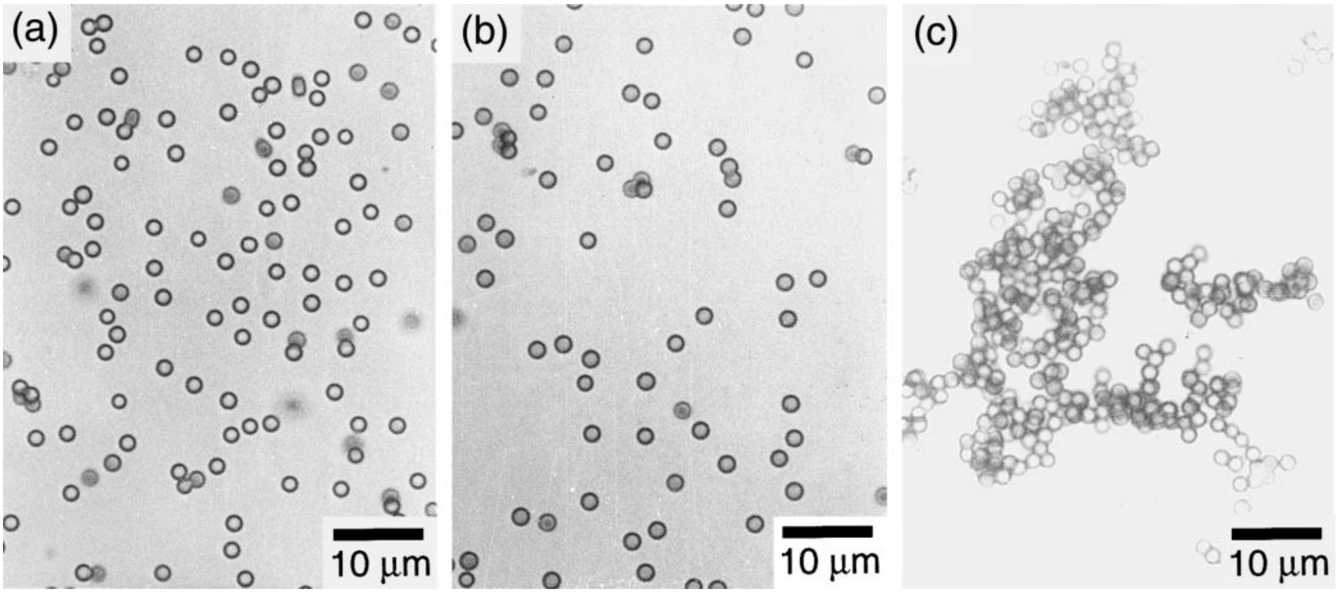


Fig. 1 Optical photographs of polystyrene (*PS*)/poly(3,5-xylidine) (*PXy*) composite particles produced by chemical oxidative seeded dispersion polymerizations of 3,5-xylidine (*Xy*) in HCl aqueous solution at different temperatures : **a** 5 °C; **b** 20 °C; **c** 35 °C

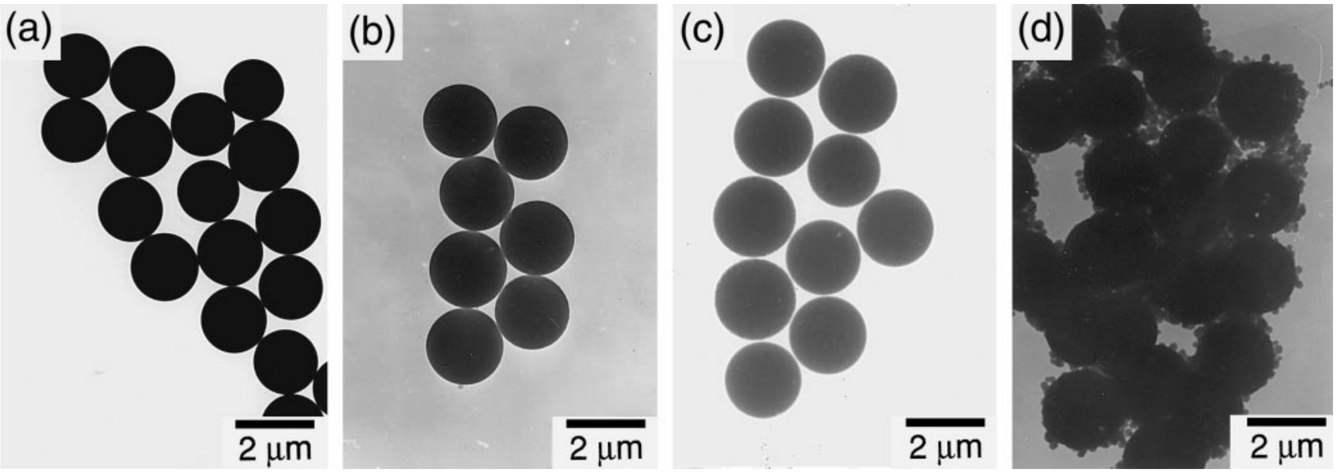


Fig. 2 Transmission electron microscope (*TEM*) photographs of **a** PS seed particles and PS/PXy composite particles produced by chemical oxidative seeded dispersion polymerizations of Xy in HCl aqueous solution at different temperatures: **b** 5 °C; **c** 20 °C; **d** 35 °C

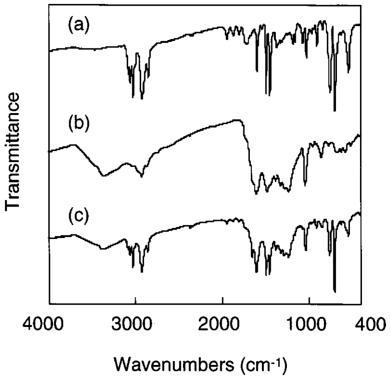


Fig. 3 FT-IR spectra of **a** PS seed particles, **b** PXy particles, and **c** PS/PXy composite particles produced by chemical oxidative seeded dispersion polymerization at 20 °C

Measurement of the conversion

The amount of unreacted Xy was measured by gas chromatography (Shimadzu Co., GC-17 A) with helium as a carrier gas. THF and BHT were used as a solvent and as a standard reagent, respectively. The temperatures of the measurement were injector, 220 °C; detector, 220 °C; column, 50 °C. The column temperature was raised linearly to 220 °C after 4 min.

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

Dried PS seed particles and PS/PXy composite particles were dipped in an epoxy matrix, cured at room temperature for 24 h and at 40 °C for 1 h before being microtomed. The ultrathin cross sections were observed with a TEM.

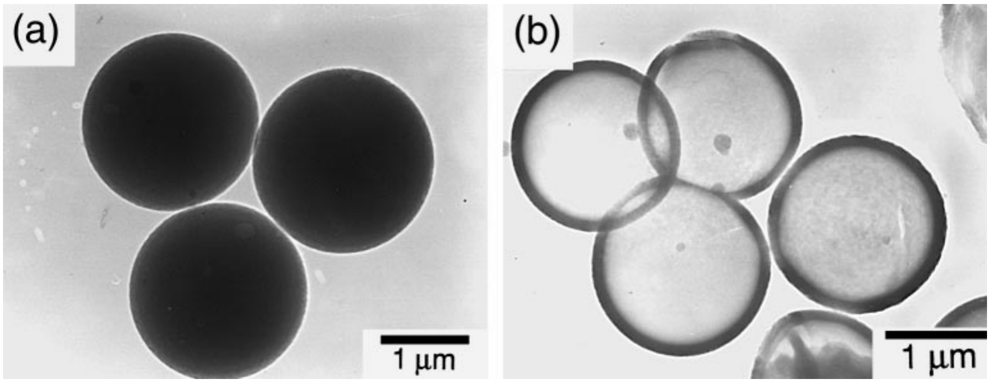
FT-IR measurement

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

Results and discussion

Optical photographs of PS/PXy composite particles produced by chemical oxidative seeded dispersion poly-

Fig. 4 TEM photographs of PS/PXy composite particles produced by chemical oxidative seeded dispersion polymerization **a** before and **b** after the extraction of PS with toluene



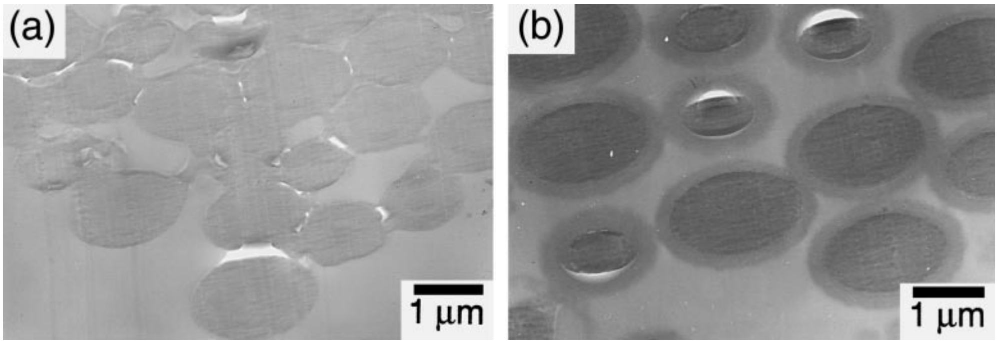


Fig. 5 TEM photographs of ultrathin cross sections of **a** PS seed particles and **b** PS/PXy composite particles produced by chemical oxidative seeded dispersion polymerization at 20°C

merizations under the condition listed in Table 2 at different temperatures before washing are shown in Fig. 1. The particles obtained at 5 and 20 °C were highly stable and a small amount of by-product PXy was observed with the optical microscope. On the other hand, the particles produced at 35 °C were coagulated. The polymerization rate of Xy increased with the increase in temperature. The coagulation at 35 °C seems to be based on the fact that too many PXy molecules are precipitated from the medium to be adsorbed completely by PS particles, which results in numerous by-product PXy particles, as shown in Fig. 2.

Figure 2 shows TEM photographs of the PS seed and PS/PXy composite particles. At 5 and 20 °C by-product PXy particles were easily removed by centrifugal washing and the surfaces of the composite particles were smooth; however, at 35 °C the PXy particles remained on the surface of the PS/PXy composite particles. The PS seed particles were spherical and monodispersed: D_n and C_v measured using the Mac Scope program were 1.56 μm and 3.8%, respectively. The PS/PXy composite particles at 5 and 20 °C were also spherical and monodispersed: D_n and C_v were 1.72 μm and 4.7%, and 1.85 μm and 4.6%, respectively. At 20 °C, the particle size was larger than that at 5 °C. This is based on the difference in the conversions of Xy at 5 and 20 °C, which were 70 and 92%, respectively. At 20 °C, the percentage of PXy introduced into the composite particles was calculated to be 81% from the densities of PS (1.04 [20]) and PXy (1.25) determined by the flotation method with NaBr aqueous solution at 30 °C. PXy was prepared under conditions similar to those listed in Table 2 except for the absence of the PS seed particles. Because the PXy sample used for the measurement was washed only with deionized water as for the PS/PXy composite particles, sulfate and chloride ions may be included, and this has an influence on the density. The percentage indicates that 88% of the PXy formed was introduced into the composite particles. The remains were by-product PXy particles and their water-soluble oligomers.

FT-IR spectra of PS seed particles, PXy and PS/PXy composite particles are shown in Fig. 3. In the spectrum of PS, the characteristic absorption peaks are 3300–3000 cm^{-1} (aromatic C-H stretching vibration), and 770–740 and 710–680 (aromatic C-H out-of-plane bending vibration). In the spectrum of PXy, the characteristic absorption peaks are 3600–3200 (N-H stretching vibration of an aromatic amine as well as of its salt), 1210–1290 (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 PS seed particles and PXy. These results indicate that PS/PXy composite particles were successfully produced.

Figure 4 shows TEM photographs before and after the extraction of PS seed particles from PS/PXy composite particles with toluene, which does not dissolve PXy but does dissolve PS, under stirring at room temperature for 6 days. In Fig. 4a, the contrast of the inside of the particles is homogeneous, whereas in Fig. 4b there is low-contrast region in the inside. The thickness of the high contrast region in Fig. 4b agreed with that calculated by subtracting the radius of the PS seed particle from that of the composite particle. This result suggested that the PS/PXy composite particles produced have a core/shell morphology with a PS core and a PXy shell.

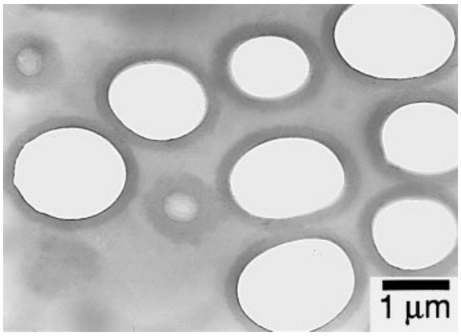


Fig. 6 TEM photograph after the extraction of PS with toluene from ultrathin cross sections of PS/PXy composite particles produced by chemical oxidative seeded dispersion polymerization at 20 °C on the TEM grid

Ultrathin cross-sections of PS seed and PS/PXy composite particles are shown in Fig. 5. The contrast in the PS seed particles is homogeneous, whereas the inside of the composite particles is comparatively darker than the surface layer. This also suggests that the PS/PXy composite particle has a core/shell morphology.

A TEM photograph of ultrathin cross sections of PS/PXy composite particles from which PS was extracted with a few droplets of toluene is shown in Fig. 6. In comparison with Figs. 5b and 6, it is obvious that the core region disappeared after the extraction of PS.

From these results, it is concluded that micron-sized monodispersed composite particles consisting of a PS core and a PXy shell were produced by chemical oxidative seeded dispersion polymerization of Xy with PS seed particles at 20 °C.

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