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ORIGINAL CONTRIBUTION

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Production of electrically conductive, core/shell polystyrene/polyaniline composite particles by chemical oxidative seeded dispersion polymerization

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Abstract Micron-sized, monodispersed, electrically conductive polystyrene (PS)/polyaniline (PAn) composite particles were produced by chemical oxidative seeded dispersion polymerization of aniline at 0 °C with 1.37-μm-sized, monodispersed PS seed particles in HCl aqueous solution, where the pH value was kept at 2.5 with a pH stat. The composite particles consisted of a PS core and a PAn shell. A pellet of the composite particles had a conductivity of 3.4×10^{-3} S/cm.

Key words Aniline · Electrically conductive · Core/shell morphology · Chemical oxidative seeded dispersion polymerization · Micron size

Introduction

Chemical oxidative polymerization of nonvinyl monomers such as pyrrole (Py) and aniline (An) has been studied in recent years [1–10]. Armes et al. [1] reported that polypyrrole (PPy) particles were produced by chemical oxidative polymerization in an aqueous medium with 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 An in HCl aqueous solution was possible with ammonium persulfate (APS) as an oxidant. Spherical and needle-shaped PAn particles were produced using various stabilizers by Vincent and Waterson [3]. In addition, there have been some studies on composite particles blended with vinyl polymers. Yassar et al. [11] synthesized polystyrene (PS)/PPy composite particles by the polymerization of Py in the presence of 0.1-μm-sized PS particles having sulfonic or carboxylic groups at the surfaces which can act as dopants for the growing conducting polymer. Beadle et al. [12] synthesized copolymer (which consists of vinyl chloride, vinylidene chloride, methyl methacrylate and acrylate)/PAn composite particles by the polymerization of An in the presence of 0.2-μm-sized copolymer particles. Xie et al. [13] synthesized poly(butadiene-*co*-styrene-*co*-2-vinylpyridine) (PBSP)/PAn composite particles by polymerization of An in the presence of 0.1-μm-sized PBSP particles. Armes and Lascelles [14] synthesized PS/PPy composite particles by the polymerization of Py in the presence of 1.57-μm-sized PS particles. They also reported that PS/PAn composite particles were successfully produced in a similar way, but did not show any experimental evidence. Cooper and Vincent [15] synthesized poly(methyl methacrylate) (PMMA)/PPy composite particles by the polymerization of Py in the presence of 0.05–0.5-mm-sized PMMA particles, but failed in synthesizing PMMA/PAn composite particles.

In a recent articles [16] we reported the synthesis of spherical and needle-shaped particles by chemical oxidative dispersion polymerization of 3,5-xylidine (Xy) with APS in aqueous medium, which were "polydisperse". Moreover, in order to control the monodispersity, seeded dispersion polymerization [17–20] was applied. Actually, micron-sized, "monodispersed", core/shell PS/poly(3,5-xylidine) composite particles were produced by the chemical oxidative seeded dispersion polymerization of Xy with 1.6-μm-sized PS seed particles [21]; however, the pellet of them had no good electrical conductivity.

In this article, we report the production of "electrically conductive", micron-sized, monodispersed, core/shell PS/PAn composite particles by chemical oxidative seeded dispersion polymerization of An, which is known to be a conductive polymer [2–5, 8–10].

Experimental

Materials

Materials guaranteed grade An, HCl, APS and 1,4-dioxane and extra reagent grade ethanol and ethylene glycol were used as received from Nacalai Tesque. Deionized water with a specific conductivity of 5×10^6 Ωcm was distilled once with a Pyrex distillator. Poly(vinyl alcohol) (PVA) was supplied by Nippon Synthetic Chemical, Osaka, Japan (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 [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-bottom flask under the optimum conditions listed in Table 1, reported in a previous article [17].

Chemical oxidative seeded dispersion polymerization

An (0.25 g) was dissolved in various concentrations of PVA aqueous solution (90 g) at pH 2.5 adjusted with HCl, in which PS seed particles (0.5 g) were dispersed. Chemical oxidative seeded dispersion polymerizations were carried out for 24 h by adding APS aqueous solutions (0.613 g/10 ml) to the dispersions. It was confirmed experimentally by gas chromatography that almost all of the An monomer existed in the aqueous medium before the polymerizations. The pH value was maintained at 2.5 using a pH stat (TOA Electronics, model HSM-10A) with 1 N KOH aqueous solution during the polymerizations. PAn particles were produced in the absence of the PS seed particles under the condition of 100 wt% PVA system. The PS/PAn composite particles and PAn particles were washed repeatedly by centrifugation before further experiment.

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

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

The particles were observed with a Nikon MICROPHOT-FXA optical microscope, a Jeol JEM-2010 transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope. The number-average diameter (D_n) and the coefficient of variation (C_v) were measured from TEM photographs using the MacScope program (Mitani Co.).

Measurement of the conversion

The amount of unreacted An was measured by gas chromatography (Shimadzu, 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 temperatures of the measurement were injector, 300 °C; detector, 300 °C; column, 220 °C.

Observations of the ultrathin cross sections of particles and pellets

For the preparation of ultrathin cross sections of particles, dried PS seed particles and PS/PAn composite particles were exposed to OsO_4 vapor at 50 °C for 1 h in the presence of 1% OsO_4 solution and were then dipped in an epoxy matrix and were cured at room temperature for 24 h and at 40 °C for 1 h before being microtomed. For the ultrathin cross sections of pellets, dried PS/PAn composite particles and the mixture of dried PS particles and PAn particles were pressed into the pellets at 500 kgf/cm^2 and were then dipped in an epoxy matrix and were cured in the same way before being microtomed. The ultrathin cross sections were exposed to OsO_4 vapor at 50 °C for 1 h in the presence of 1% OsO_4 solution. The ultrathin cross sections were observed with the TEM.

Fourier transform IR measurement

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

Measurement of conductivity

The electrical conductivity of the dried particles was determined on pressed pellets at room temperature using the conventional four-point-probe technique with a Loresta-GP MCP-T600 (Mitubishi Chemical Co.).

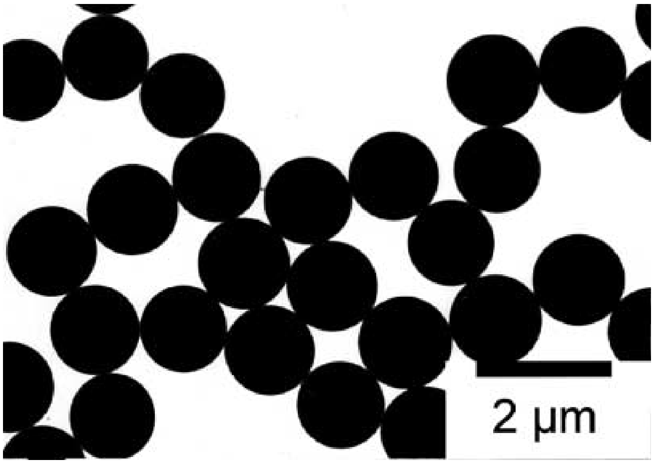


Fig. 1 Transmission electron microscopy (*TEM*) photograph of polystyrene (*PS*) seed particles produced by dispersion polymerization

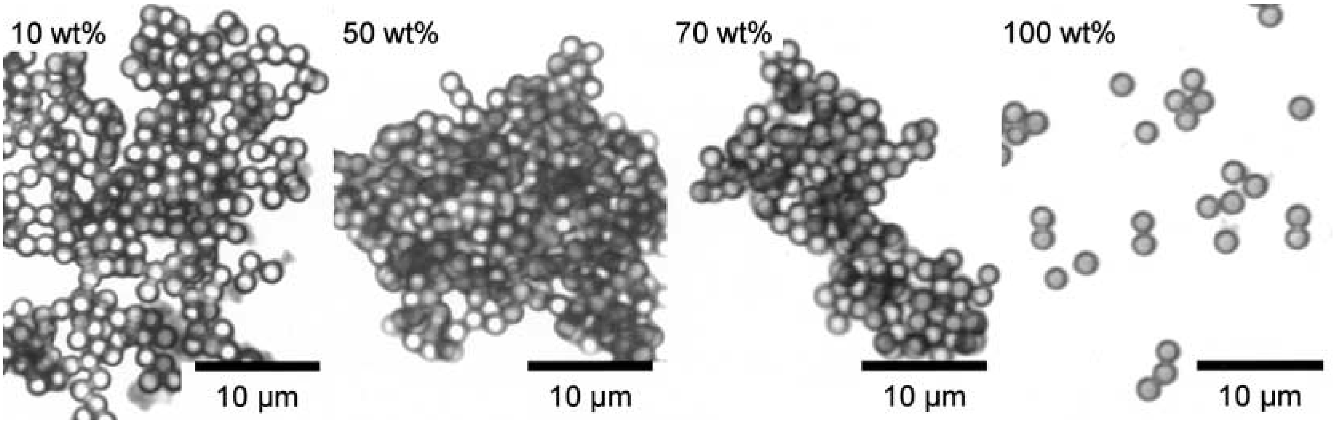


Fig. 2 Optical photographs of PS/polyaniline (*PAn*) composite particles produced by chemical oxidative seeded dispersion polymerizations of aniline in HCl aqueous solution with different amounts of poly(vinyl alcohol) (*PVA*) (weight percentage based on PS seed particles)

Measurement of the composition of PS/PAn composite particles

^{1}H NMR spectra were obtained with a Bruker DPX250 NMR spectrometer operating at 250 MHz for protons with 200 scans, in 5-mm NMR tubes. PS seed particles or PS/PAn composite particles were dispersed in pyridine-d_5 dissolving 2-methoxynaphthalene as a standard reagent, which does not dissolve PAn but which does dissolve PS. From the calibration curve (weight ratio versus intensity peak ratio of PS/2-methoxynaphthalene), the amount of PAn in the composite particles was determined.

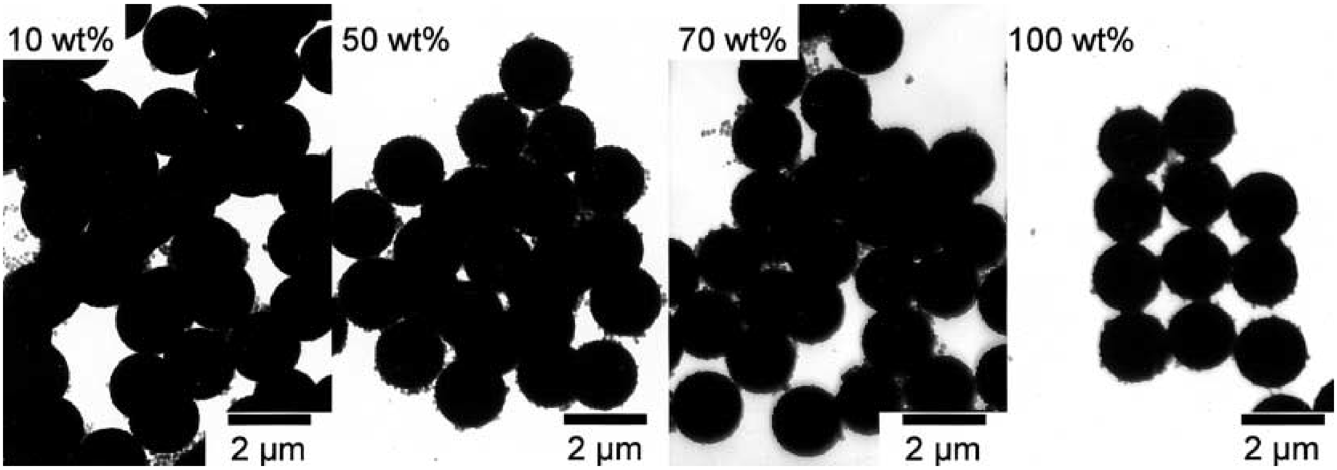
Results and discussion

A TEM photograph of the PS seed particles produced by dispersion polymerization 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 PS/PAn composite particles produced by the chemical oxidative seeded dispersion polymerizations of An with APS as an oxidant at different PVA concentrations (weight percentage based on PS seed particles: 10, 50, 70, 100) at pH 2.5, before washing, are shown in Fig. 2. The composite particles produced in the 100 wt% PVA system were stably dispersed throughout the polymerization; on the other hand, the other particles coagulated. The coagulation seems to be based on the exhaustion of PVA to stabilize the composite particles by the preparation of numerous by-product PAn particles. In the latter stage of the polymerizations, the pH electrode was covered by PAn film, which might be caused by the ionic interaction between the pH electrode having negative charge and PAn having positive charge. This affects pH control of the systems [22, 23]. Actually after the polymerizations, the pH values of the systems were below 2.5 (measured with the PAn film-removed pH electrode).

TEM photographs of the PS/PAn composite particles after centrifugal washing are shown in Fig. 3. In the cases of 10, 50 and 70 wt% PVA systems, all the composite particles coagulated during the polymeriza-

Fig. 3 TEM photographs of PS/PAn composite particles produced by chemical oxidative seeded dispersion polymerizations of aniline in HCl aqueous solution with different amounts of PVA (weight percentage based on PS seed particles)



tions and by-product PAn particles were observed on the coagulated composite particles. By-product PAn particles dispersed in the medium could be easily removed by centrifugal washing, but those adsorbed on the coagulated composite particles could not be removed. In the case of the 100 wt% PVA system, the composite particles dispersed stably during the polymerization and few by-product PAn particles were observed after washing. The PS/PAn composite particles produced in the 100 wt% PVA system were micron-sized and monodisperse: D_n, 1.68 μm; C_v, 3.6%. The weight percentage of the PAn component in the composite particles was determined to be 17% from NMR measurements, which corresponds to 40% of the total amount of An put in the system. The conversion of An was 76%, which was determined from the amount of unpolymerized An measured by gas chromatography. The amount of by-product PAn was calculated to be 36% of the total An. Since the composite particles used for the NMR measurement were washed only with deionized water, sulfate and chloride ions may be included in PAn as dopant anions [5]. Accordingly, the authors point out that the percentages of PAn in the composite particles and the by-product PAn have errors.

FT-IR spectra of PS seed particles, PAn and PS/PAn composite particles are shown in Fig 4. In the spectrum of PS, the characteristic absorption peaks were 3150 cm^{-1} (aromatic C–H stretching vibration) and 755 and 700 cm^{-1} (aromatic C–H out-of-plane bending vibration). In the spectrum of PAn, the characteristic continuous absorption was observed from 4000–1800 cm^{-1} (this adsorption contains N–H stretching vibration of an aromatic amine as well as of its salt) [24–26], and the characteristic absorption peaks were 1300 cm^{-1} (C–N stretching vibration) and 1560 cm^{-1} (C=N stretching vibration). Comparing the spectrum of the PS/PAn composite particles with the spectra of the PS and PAn particles, the vibration bands observed for the PS/PAn composite particles can be reasonably assigned to PS seed particles and PAn. This result indicates that the PS/PAn composite particles were successfully produced.

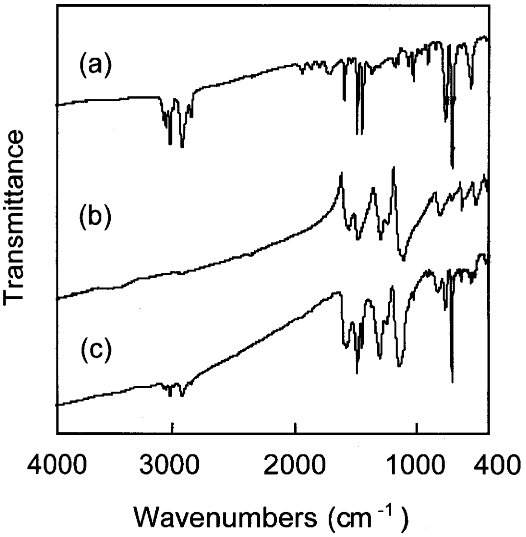
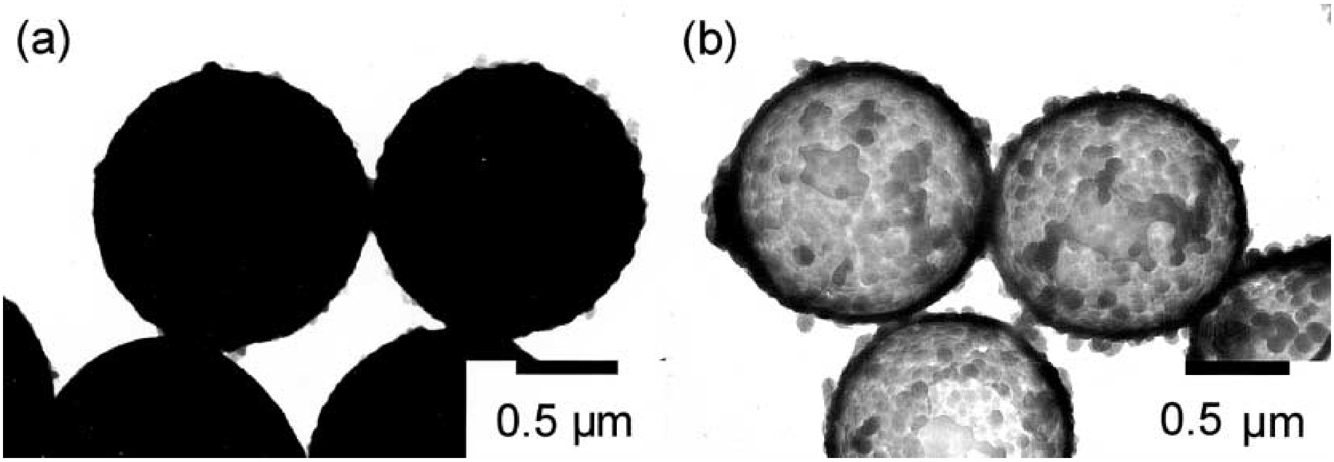


Fig. 4 Fourier transform IR spectra of PS seed particles (*a*), PAn particles (*b*), and PS/PAn composite particles (*c*) produced by chemical oxidative seeded dispersion polymerization in the 100 wt% PVA system

TEM photographs before and after the extraction of PS seed particles from PS/PAn composite particles with toluene, which does not dissolves PAn but which does dissolve PS under stirring at room temperature for 6 days, are shown in Fig. 5. In Fig. 5a, the contrast in the composite particles is homogeneous, whereas in Fig. 5b there is a low-contrast region in the inside. The thickness of the high-contrast region in Fig. 5b agreed with that calculated by subtracting the radius of the PS

Fig. 5 TEM photographs of PS/PAn composite particles produced by chemical oxidative seeded dispersion polymerization in the 100 wt% PVA system **a** before and **b** after the extraction of PS with toluene



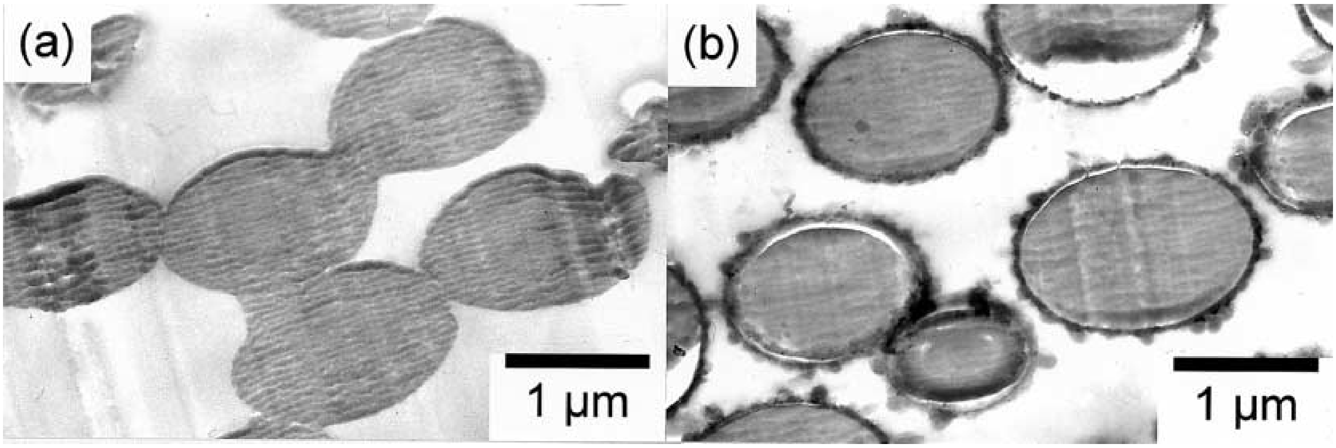


Fig. 6 TEM photographs of ultrathin cross sections of **a** PS seed particles and **b** PS/PAn composite particles produced by chemical oxidative seeded dispersion polymerization in the 100 wt% PVA system

seed particle from that of the composite particle. This result suggests that the PS/PAn composite particles had a core/shell morphology with a PS core and a PAn shell.

Ultrathin cross sections of PS seed and PS/PAn composite particles are shown in Fig. 6. The contrast in the PS seed particles was homogeneous, whereas the surface layer of the composite particles was comparatively darker than the inside. A TEM photograph after extraction of PS from the ultrathin cross sections of PS/PAn composite particles with a few droplets of toluene is shown in Fig. 7. In comparison with Fig. 6b, it is obvious that the core region disappeared after the extraction of PS. This also indicates that the PS/PAn composite particle has the core/shell morphology.

Table 2 Conductivities (measured using the conventional four-point-probe technique) of the pellets of PS seed particles, the mixture of PS particles and polyaniline (*PAn*) particles [PS/PAn (5/1, w/w)] and PS/PAn (5/1, w/w) composite particles

Ingredients	Conductivity (S/cm)
PS particles	~0[a]
PAn particles	4.2×10^{-2}
Mixture of PS particles and PAn particles	~0[a]
PS/PAn (5/1, w/w) composite particles	3.4×10^{-3}

[a] Lower limit of measurable conductivity, 10^{-8} S/cm

The conductivities of various pellets of PS seed particles, PAn particles, the mixture of PS and PAn particles (PS/PAn: 5/1, w/w) and PS/PAn (5/1, w/w) composite particles are given in Table 2. The PAn particles were sub-micron-sized and had the form of an ellipse as shown in Fig. 8: D_n and C_v were 177 nm and 24.2%, respectively. The conductivity of the PS seed particles was lower than the limit of measurable

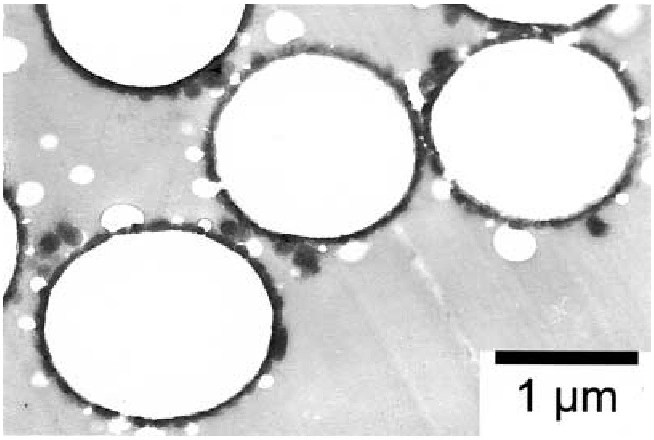


Fig. 7 TEM photograph after the extraction of PS with toluene from ultrathin cross sections of PS/PAn composite particles produced by chemical oxidative seeded dispersion polymerization in the 100 wt% PVA system on the TEM grid

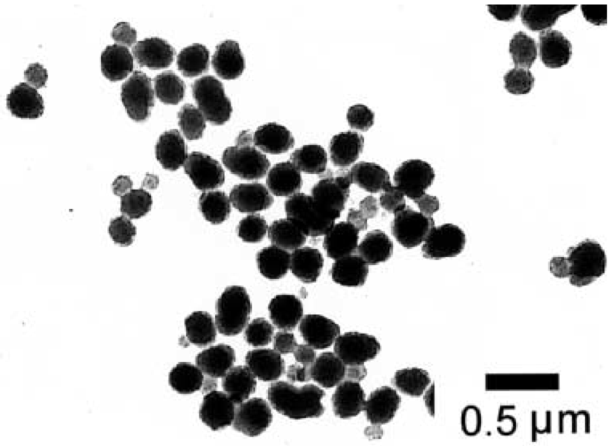


Fig. 8 TEM photograph of PAn particles prepared under the same conditions as the production of PS/PAn composite particles in the 100 wt% PVA system except for the absence of the PS seed particles

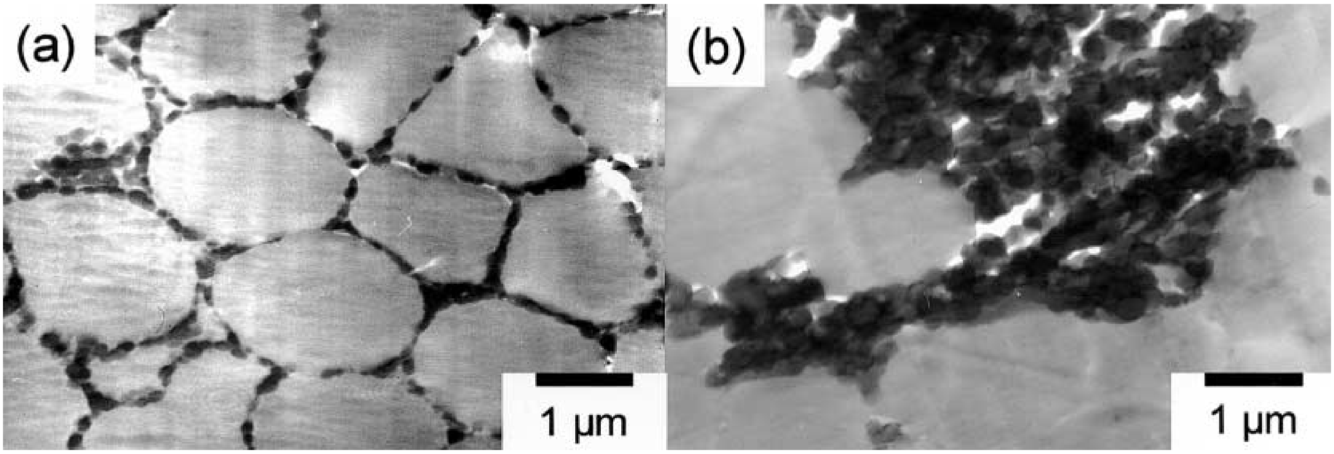
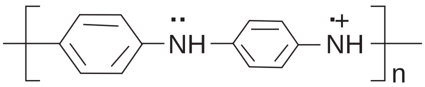


Fig. 9 TEM photographs of ultrathin cross sections of **a** the pellets of PS/PAn (5/1, w/w) composite particles and **b** the mixture of PS and PAn particles; PS particles/PAn particles (5/1, w/w)

conductivity, 10^{-8} S/cm, and that of the PAn particles was 4.2×10^{-2} S/cm. The conductivity of the mixture of PS seed particles and PAn particles was lower than 10^{-8} S/cm, as well as that of the PS seed particles. This indicates that the continuous phase consists of PS component and that the PAn component disperses separately in the mixture. The conductivity of the PS/PAn composite particles having the same PS/PAn weight ratio as that of the mixture was 3.4×10^{-3} S/cm, which was only one order of magnitude lower than that of the PAn particles. The high conductivity indicates that a continuous phase in the pellet consists of green protonated emeraldine formed PAn [27–30], which is known to be electrically conductive. Green protonated emeraldine has the following structure:



As already described, the conversion of An in the chemical oxidative seeded dispersion polymerization for the 100 wt% PVA system was 76%, and this accords well with the report [27] that the conversion of An in the formation of green protonated emeraldine at an APS/An molar ratio of 1/1 was 80%.

TEM photographs of ultrathin cross sections of the pellets of PS/PAn composite particles and of the mixture of PS and PAn particles are shown in Fig. 9. In the pellet of PS/PAn composite particles, interfacial conductive paths consisting of the PAn shells were observed, and efficient charge transport through the material can occur without significant interference from the underlying electrically insulating PS component. Even after the extraction of PS from ultrathin cross sections of the pellet of PS/PAn composite particles with a few droplets of toluene, conductive paths remain and ranged continuously, as shown in Fig. 10. Armes and Lascelles [14] represented the model of charge transport between PS/PPy composite particles at the microscopic level, but there was no experimental evidence. On the other hand, as shown in Fig. 9b, the conductive PAn particles aggregated and did not range, which clearly indicates that efficient charge transport cannot occur.

From these results, it is concluded that electrically conductive, micron-sized, monodispersed composite particles consisting of a PS core and a PAn shell were produced by chemical oxidative seeded dispersion polymerization of An with PS seed particles at 0 °C.

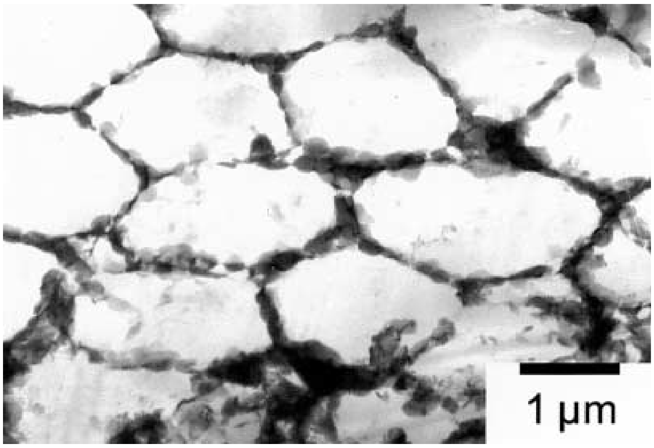


Fig. 10 TEM photograph after the extraction of PS with toluene from ultrathin cross sections of the pellet of PS/PAn (5/1, w/w) composite particles

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