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ORIGINAL CONTRIBUTION

Preparation of polystyrene/poly (4-butyltriphenylamine) composite particles by chemical oxidative seeded dispersion polymerization

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Abstract Polystyrene (PSt)/poly (4-butyltriphenylamine; PBTPA) composite particles was prepared by a chemical oxidative seeded dispersion polymerization of (4-butyltriphenylamine) with PSt seed particles that were prepared by nonaqueous dispersion polymerization of styrene. Monodisperse composite particles were obtained when the ratio of monomer to seed, the rate of monomer feed, and poly (*N*-vinyl pyrrolidone; PVP) concentration was appropriately selected. The introduction of PBTPA was confirmed by the presence of the characteristic absorption band attributed to PBTPA from a Fourier transform infrared spectra. The solvent extraction with ethyl acetate revealed that composite particles consisted of PSt core and PBTPA shell. Then two-dimensional arrays of composite particles were also fabricated.

Keywords Photoconductive polymer · Chemical oxidative seeded dispersion polymerization · Composite particle · 4-butyltriphenylamine

Introduction

Nonaqueous phase dispersion polymerization (NAD) affords monodispersed polymer particles [1]. Polymer particles prepared by NAD polymerization have been widely used in industrial applications, such as standard calibration, paint, and so on.

The dispersion of conducting polymer provides processibility, nevertheless the insolubility of the most of conducting polymers, and in recent years, chemical oxidative dispersion polymerization of monomers such as pyrrole, aniline, aniline derivatives has been investigated [2–12].

Armes et al. [2] reported that polypyrrole particles were obtained by chemical oxidative polymerization in aqueous medium with ferric chloride as an oxidant, and the electrical conductivity was measured for pellets. Polypyrrole particles were prepared by oxidative dispersion polymerization using PVA or functionalized with pyrrole moiety as a dispersant in the aqueous medium in the presence of ferric chloride as an oxidant. They mentioned that the amount of oxidant tend to increase the conductivity [5]. Riede et al. [6] reported that polyaniline dispersion was fabricated by oxidative polymerization utilizing poly(*N*-vinyl pyrrolidone; PVP) or hydroxylropylcellulose as a dispersant. The particle formation was confirmed by light scattering measurements. They stated that the nature of the particle formation is similar in all case and formation of particles is faster in the presence of polymeric stabilizers. Okubo et al. [7] carried out the oxidative dispersion polymerization of 3,5-xylidine (Xy) at 20 °C with PSt particles used as the seed. They also reported needle-like crystalline particles of PXy [8]. Monodispersed composite particles showed excellent dispersion stability. The composite particles consisted of a PSt core and PXy shell were confirmed by the solvent extraction with toluene.

Recently, we reported that PBTPA was simply prepared by chemical oxidative polymerization using ferric chloride as an oxidant. PBTPA showed the excellent photoconductivity compared with a conventional poly (*N*-vinylcalbazole) [13]. Triphenylamine derivatives have been used as hole-transporting materials in organic photoconductors and electroluminescent device [14, 15]. Although PBTPA is a

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promising material as an organic semiconductor, until now, it is difficult to obtain the PBTPA monodispersed particles by a dispersion polymerization.

In this study, composite particles are prepared by chemical oxidative seeded dispersion polymerization of PBTPA using PSt seed particles.

Experimental

Materials

All the reagants, unless stated otherwise, were purchased from Wako Pure Chemical Industries. Distilled and deionized water was used. Styrene was purified by distillation under reduced pressure and stored in a refrigerator. Xylene was distilled under atmospheric pressure. Other chemicals were used without further purification except otherwise noted.

Preparation of 4-*n*-butyltriphenylamine monomer

4-*n*-butyltriphenylamine (BTPA) were synthesized as described in [13]. Diphenylamine, 1-bromo-4-butylbenzene, palladium acetate (Aldrich Chem.), *t*-BuONa, P(*t*-Bu)$_3$ (HokkoChem.), and xylene were added into a three-necked 300-ml round-bottom flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet. The reaction was carried out at 120 °C for 3 h under a nitrogen blanket.

Preparation of seed particles

Micron-sized monodispersed PSt seed particles were obtained by NAD polymerization of styrene in ethanol or a mixture of ethanol and water [16]. Styrene, 2,2-azobis (isobutyronitrile), PVP K-30, sodium di(2-ethylhexyl)sulfosuccinate (Tokyo Chem.), ethanol (or ethanol-water) were added to 300-ml round-bottom flask equipped with an anchor type stirrer, condenser (nitrogen inlet) and then stirred at 80 rpm at 70 °C for 24 h under a nitrogen blanket. Obtained PSt seed particles were washed repeatedly with ethanol by centrifugation before further use. Table 1 shows the recipe for seed particles with a different diameter.

Table 1 Preparation of monodispersed PSt seed particles by NAD polymerization

Ingredients	Seed 1	Seed 2	Seed 3
Styrene (g)	13.5	13.5	13.5
2,2′-Azobis(isobutyronitrile) (g)	1.35	1.35	1.35
PVP (g)	1.51	1.51	1.51
Bis(2-ethylhexyl) ester of sodium sulfosuccinic acid (g)	0.431	0.431	0.431
Ethanol (g)	71.0	75.0	78.9
Water (g)	10	5	0

N$_2$; 70 °C; 24 h; 80 rpm

Table 2 Standard recipe of PSt/BTPA composite particles by chemical oxidative seeded dispersion polymerization at 50 °C, 24 h

Ingredients		
PSt seed particles (g)	0.755	
BTPA (g)		0.755[a]
Ferric chloride (g)	3.24	
PVP (g)	0.0755	
Ethanol (ml)	18.4	3.16[a]
Chloroform (ml)	8.63	1.48[a]

[a] Solution of BTPA in ethanol/chloroform (4.64 g) was added

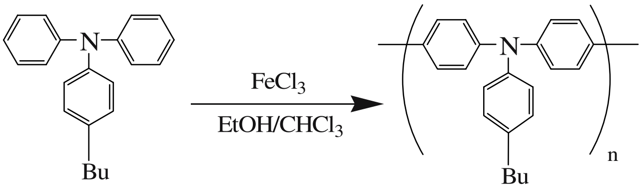
Chemical oxidative seeded dispersion polymerization

In a three-necked 50-ml round-bottom flask equipped with a condenser and a nitrogen inlet, PSt seed particles were dispersed in ethanol/chloroform [4/1(V/V)] containing ferric chloride and PVP. Then, monomer solution was fed to the reaction vessel after the temperature was reached at 50 °C. Standard recipe is shown in Table 2. Feeding rate was controlled by a syringe pump. Chemical oxidative seeded dispersion polymerizations were carried out for 24 h after feeding under a nitrogen blanket. Composite particles were washed repeatedly by centrifugation with ethanol and HCl mixture. Polymerization route of 4-butyltriphenylamine is shown in Scheme 1.

Characterizations

Morphology and particle size of the seed or composite particles were investigated by scanning electron microscopy (SEM; Philips XL 30) with a 15 degree tilt. The average diameter of the seed or composite particles and size distribution were determined by the direct measurement of more than 200 particles in SEM photographs.

Infrared (IR) spectra of composite particle were measured with Fourier transform IR (FT-IR) spectrometer (Jasco, FT/IR-460 plus). The resolution for all spectra was 4 cm^{-1}. Samples were deposited on the surface of a KBr plate by casting from a chloroform solution.



Scheme 1 Polymerization of 4-buthyltriphenylamine

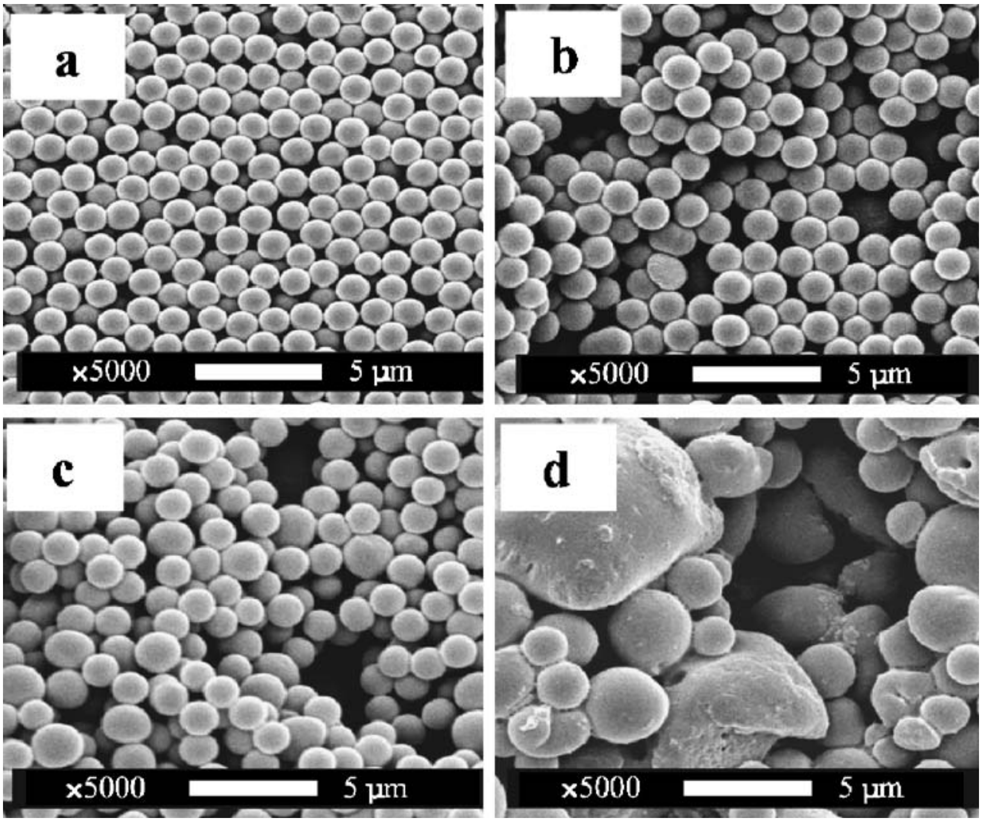


Fig. 1 SEM photographs of PSt/BTPA composite particles produced by chemical oxidative seeded dispersion polymerization with different amount of BTPA (weight ratio based on PSt seed): **a** seed particles; **b** BTPA/PSt=0.5; **c** BTPA/PSt=1.0; **d** BTPA/PSt=2

Composite particles dispersion after purification was dried under vacuum at room temperature. Composite particles were dispersed in ethyl acetate. Ethyl acetate dissolves PSt but does not dissolve PBTA at room temperature.

Dispersion of composite particles in ethanol was prepared with a concentration of 5 wt.%. Two-dimensional arrays of composite particles were fabricated as described in [17]. The tapered cell was made using a pair of glass substrates, and wedge geometry was formed using spacers with thickness of 0.2–0.4 mm. After the tapered cell filled with the suspension, the drying process of suspension was observed from the thicker edge. After the completion of the drying process, a single layer of the array of composite particles was observed on the lower glass. Array structure was evaluated with SEM observation and light diffraction.

Results and discussion

Monodispersed seed particles with an average diameter 1.25 μm and a coefficient of variation (CV) value 6.31% was obtained by dispersion polymerization under the conditions listed in Table 1 (Seed 1). A SEM photograph is shown in Fig. 1a. SEM photographs resulting composite particles in Fig. 1 show BTPA/seed ratio effects on particle morphology. Figure 1b and c show that spherical monodispersed particles were obtained with a BTPA/PSt ratio from 0.5 to 1. On the other hand, particles obtained with a BTPA/PSt ratio of 2 were coagulated and nonspherical (Fig. 1d). The nonspherical and coagulated particles seem

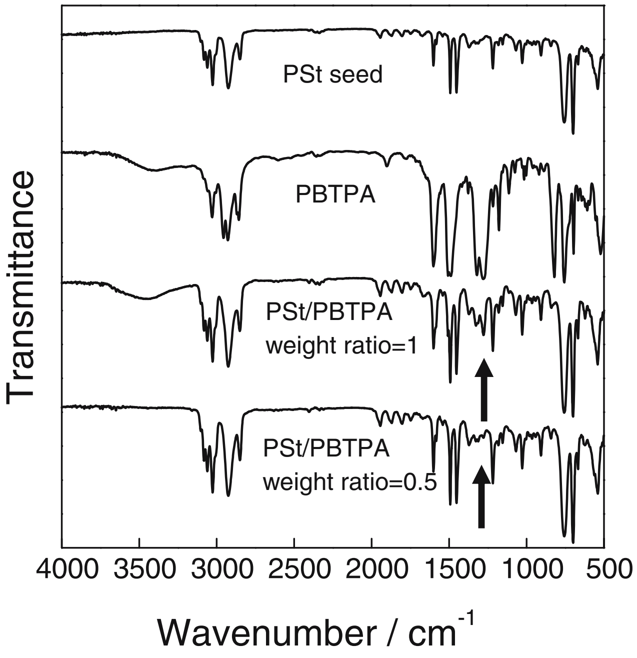


Fig. 2 FT-IR spectra of PSt seed, PBTPA, PSt/PBTPA composite particles

to lose the stability during the reaction because too many PBTPA chains are precipitated from the medium to be adsorbed completely by the seed particles. The other possibility is that the stability of the seed particles before reaction was lost with the increase in ferric chloride in the reaction system. Average diameter and CV value of PSt/PBTPA composite particles with PSt/PBTPA weight ratio of 0.5 and 1 are 1.35 μm and 6.83%, 1.42 μm and 10.8%, respectively. With a PSt/PBTPA ratio of 1, the particle size was slightly larger than that with the PSt/PBTPA ratio of 0.5.

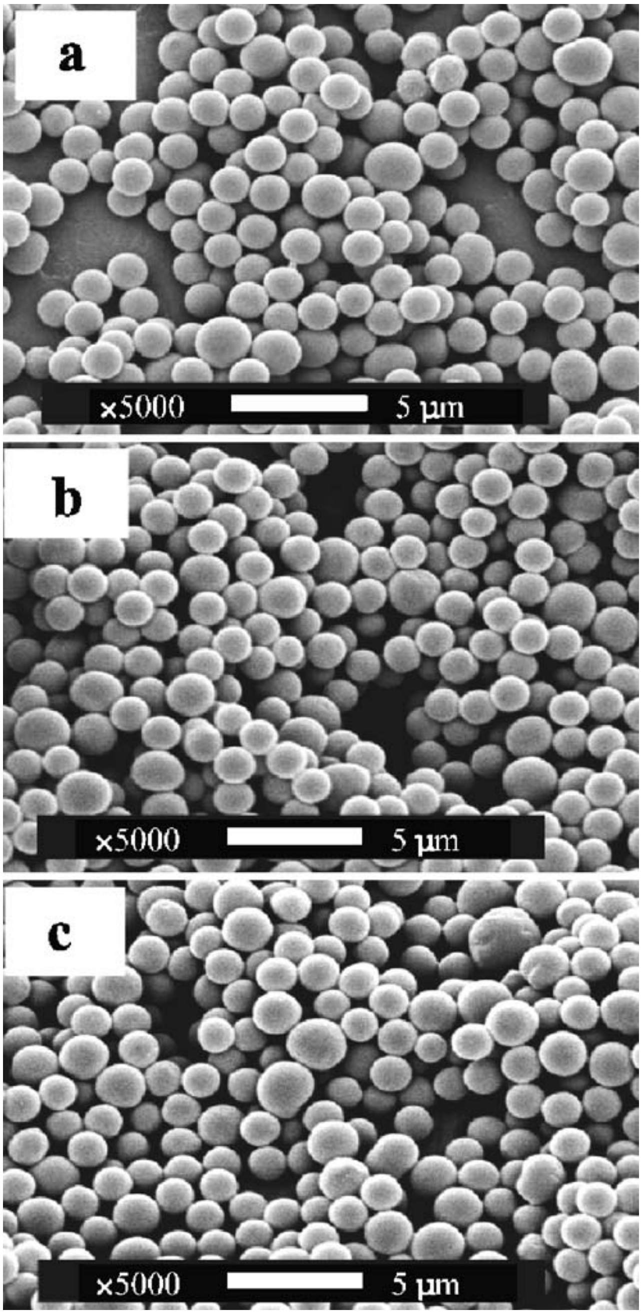


Fig. 3 SEM photographs of PSt/BTPA composite particles with different monomer feed rate: **a** 0.3 ml/min ; **b** 0.05 ml/min; **c** 0.025 ml/min

Typical FT-IR spectra of PSt seed, PBTPA, PSt/PBTPA composite particles are shown in Fig. 2. Common absorption bands to PSt and PBTPA are 3,140–2,980 cm^{-1} attributed to aromatic C–H vibration, 2,000–1,800 cm^{-1} to a number of weak combination and overtone, 1,600–1,400 cm^{-1} to aromatic ring vibration, 800–750 cm^{-1} to aromatic C–H out of plane bending. In the spectrum of PBTPA and composite particles, characteristic absorption band is observed at 1,320–1,280 cm^{-1} attributed to C–N stretching vibration (as indicated by arrows). The spectrum

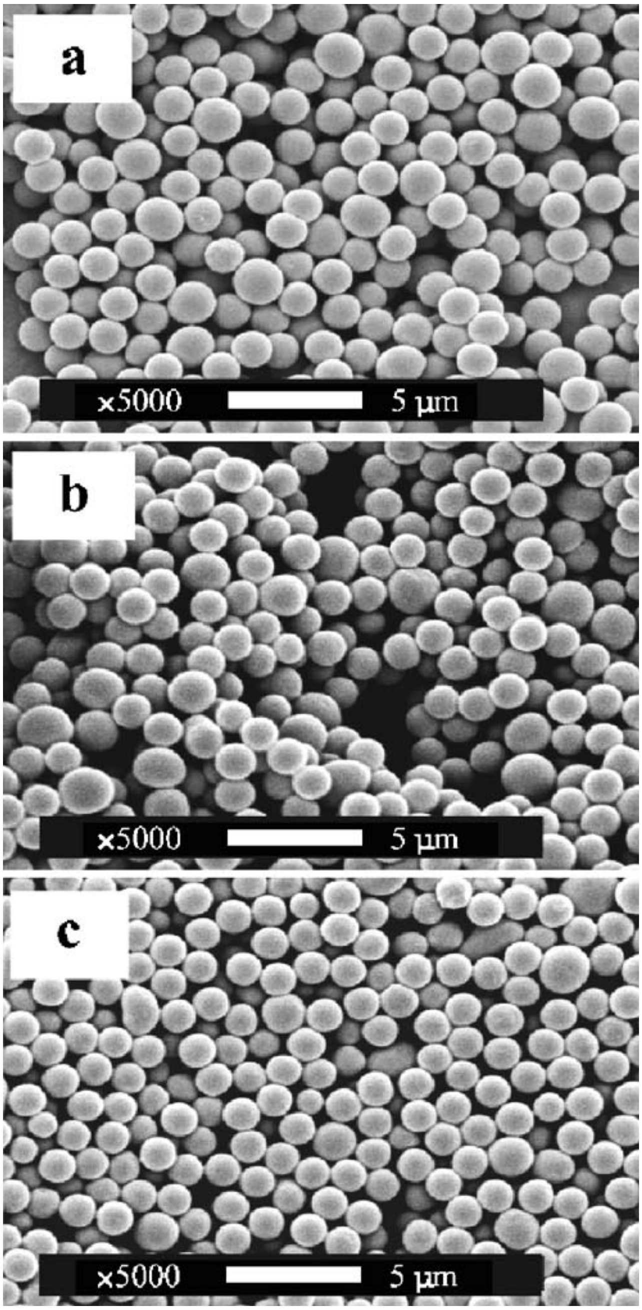


Fig. 4 SEM photographs of PSt/BTPA composite particles with different PVP concentration: **a** 2.5 wt.%; **b** 5 wt.%; **c** 10 wt.%

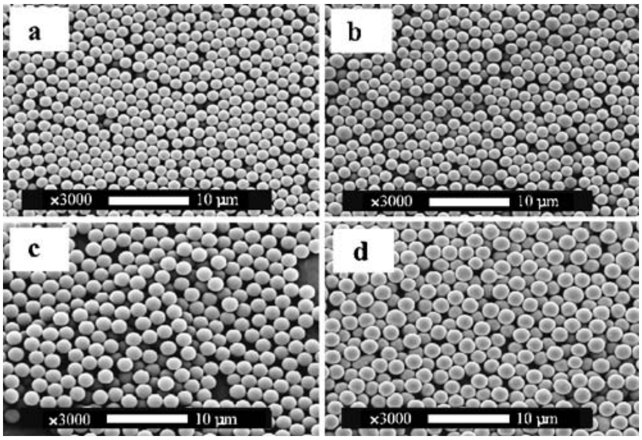


Fig. 5 SEM photographs of PSt/BTPA composite particles with different seed particles: **a** seed 2; **b** composite particles using seed 2; **c** seed 3; **d** composite particles using seed 3

of composite is almost the same as that obtained by superimposing each spectrum of PSt and PBTPA, and the absorption band can be assigned to PSt and PBTPA. This result indicates that PSt/PBTPA composite particles were successfully synthesized. However, in the spectrum of composite particles (weight ratio=0.5) the characteristic absorption band due to C–N stretching vibration bands are not observed clearly. This is due to the fact that relative amount of BTPA is small in the composite particles. Following experiments were carried out with a BTPA/PSt ratio of 1. At first, the effect of monomer feed rate was investigated on average diameter, size distribution, and particle shape.

Figure 3 shows the SEM of composites prepared with various feed rates. In our investigation, the rate of 0.05 ml/min was most appropriate for monodispersity, and the faster 0.3 (ml/min) or slower (0.025 ml/min) rates afforded polydispersed nature to the resulting particles. In the case of feed rates 0.3 (1.56 µm and 15.3%), 0.025 ml/min (1.52 µm and 12.7%), composite particles were rather polydispersed compared with 0.05 ml/min. At 0.3 ml/min, the production rate of PBTPA was so fast that too many PBTPA chains are precipitated from the medium to be adsorbed completely by the seed particles. In the case of below 0.025 ml/min, generation of nucleation stage was long. Nucleation and growth process existed competitively throughout the feeding. Therefore, long feeding time leads to polydispersed particles. Tseng et al. [18] stated that the generation rate of nuclei was important to obtain the monodispersed particles.

SEM photographs of composite particles prepared at different PVP concentration (weight percentage based on PSt seed plus BTPA monomer: 2.5, 5, 10) are shown in Fig. 4. Average diameter and CV value of PSt/PBTPA composite particles with PVP concentration of 2.5 and 10 wt.% are 1.45 µm and 9.29%, 1.34 µm and 9.41%, respectively. The average diameter of composite particles decreases gradually with increasing PVP concentration. The composite particles obtained at 2.5, 5, and 10 wt.% were highly stable. However, the composite particles. were coagulated where the concentration of PVP was less than 2.5 wt.%. It seems that more than 2.5 wt.% PVP is necessary to stabilize the dispersion of composite particles.

The effect of the diameter of a seed particle was studied using PSt seed particles (D_n and CV were 1.51 µm and 4.98% and 1.90 µm 4.41%, respectively). SEM photographs of composite particles obtained using different seed particles are shown in Fig. 5. Monodispersed seed particles were obtained by dispersion polymerization under the conditions listed in Table 2 (Seed 2, Seed 3). The composite particles for Seed 2 were monodispersed with an average diameter of 1.71 µm and a CV value of 8.91%, Seed 3 also monodispersed with 2.12 µm and 8.52%. In the case of seed 2 and 3, almost the same tendency was observed as for the above mentioned for seed 1.

Table 3 summarizes the experimental results for chemical oxidative seeded dispersion polymerization. The volume ratio of PBTPA in a composite particle was calculated assuming that the density of PSt and PBTPA was equal. For the preparation of monodispersed particles, the ratio of a BTPA monomer could not exceed two. When

Table 3 Experimental conditions and results for chemical oxidative seeded dispersion polymerization

Run	Seed particle (µm)	BTPA/PSt ratio	Feed rate (ml/min)	PVP concentration (wt.%)	PBTPA/PSt composite particle (µm)	CV value (%)	PBTPA/(PBTPA+PSt) volume ratio
1	1.25	0.5	0.05	5	1.35	6.83	0.21
2	1.25	1	0.05	5	1.42	10.8	0.32
3	1.25	1	0.025	5	1.52	12.7	0.44
4	1.25	1	0.3	5	1.56	15.3	0.49
5	1.25	1	0.05	2.5	1.45	9.29	0.36
6	1.25	1	0.05	10	1.34	9.41	0.19
7	1.51	1	0.05	2.5	1.71	8.91	0.31
8	1.90	1	0.05	2.5	2.12	8.52	0.28

the ratio was less than one, the volume ratio of PBTPA was controlled by changing the feed rate of monomer, keeping the resulting monodispersed particles (Run 1 and 2). The feeding rate of the monomer solution and PVP concentration were optimized at 0.05 ml/min and 2.5 wt.%, respectively. It is considered that excess amount of PVP deactivated oxidant because of the complex formation resulting in a low conversion or low PBTPA volume ratio [3]. Particle size could be controlled by changing the size of seed particles at least in the range of diameter we examined.

Figure 6a shows a SEM photograph after the solvent extraction of PSt seed particles from composite particles with ethyl acetate. Ethyl acetate does not dissolve PBTPA but does dissolve PSt. Compared with composite particles, average diameter and CV value did not change after extraction (particles, 2.12 μm, 8.52%, after extraction, 2.09 μm, 7.66%). Then composite particles were crushed with a glass plate. Deformed or broken hollow particles were observed in Fig. 6b. This result suggested that composite particles have core-shell morphology with PSt core and PBTPA shell.

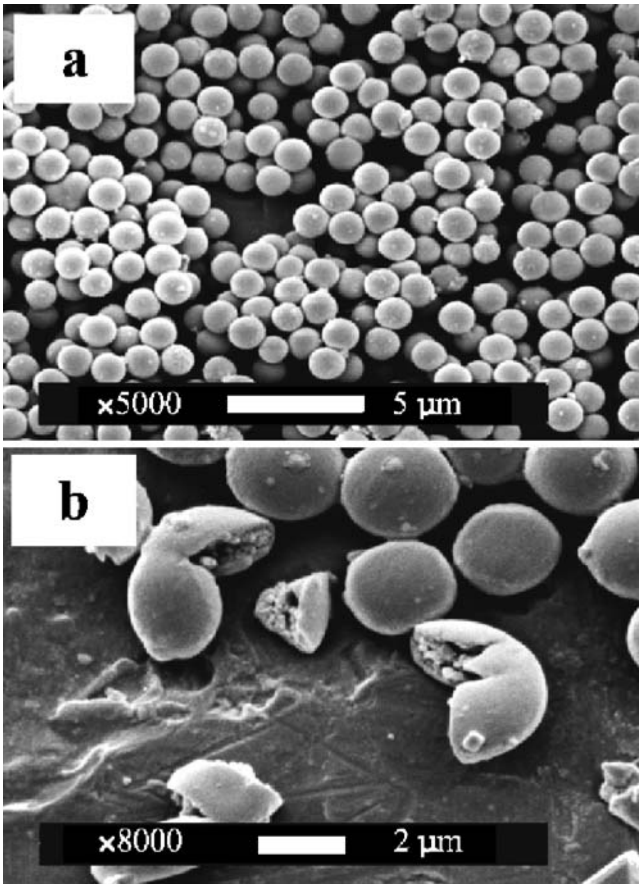


Fig. 6 SEM photographs of PSt/BTPA composite particles after solvent extraction with ethyl acetate: **a** after extraction; **b** after deformation

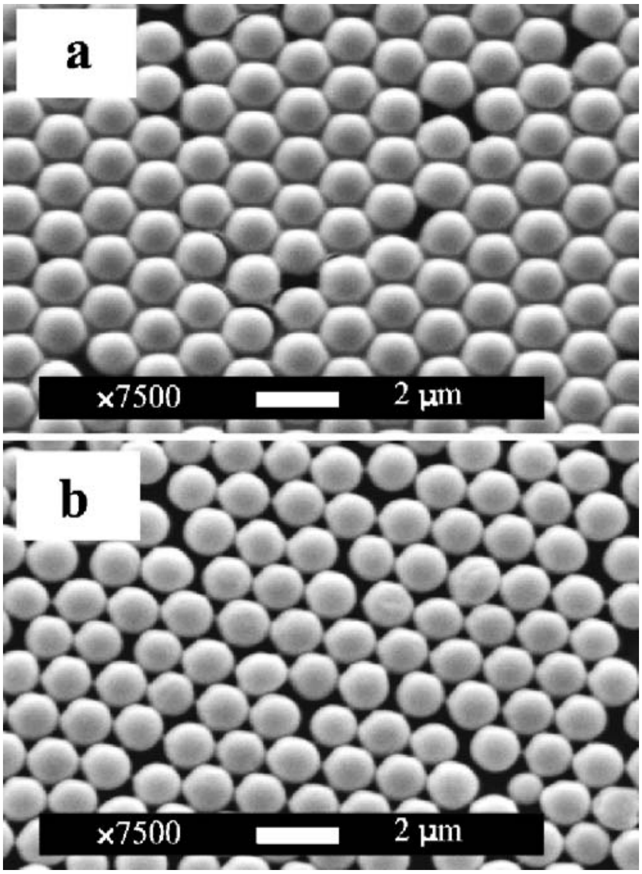


Fig. 7 SEM images of array: **a** seed 1; **b** composite particles using seed 1

Figure 7 shows the SEM image of array on glass substrate. Hexagonal close packed arrays were observed for both seed 1 and composite particles. Vacancies and dislocations mainly because of particles with larger diameter are observed. Diffraction patterns are shown in Fig. 8. The origin of this hexagonal pattern is explained in [17]. Spot size of composite particles is slightly large and fuzzy compared with seed 1. These differences result from polydispersity of composite particle and lattice expansion.

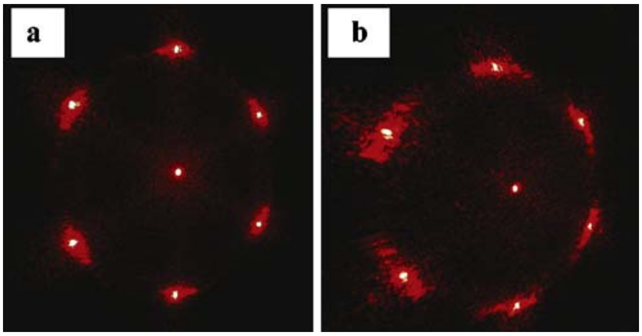


Fig. 8 Photographs of diffraction spots of arrays: **a** seed 1; **b** composite particles using seed 1

Conclusion

From these results, it is concluded that monodispersed composite particles consisting of PSt core and PBTPA shell were produced by chemical oxidative seeded dispersion polymerization. Size of composite particle can be controlled by changing seed particles while maintaining the monodispersity and dispersion stability.

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