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SEED DISPERSION POLYMERIZATION TO MICRON-SIZE MONODISPERSE POLYMER PARTICLES

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ABSTRACT

Seed dispersion polymerization of methyl methacrylate (MMA) in the presence of monodisperse PMMA particles was carried out in an aqueous methanol using poly(methacrylic acid) stabilizer. The polymerization using 2.5 μm-sized seed particles gave monodisperse PMMA particles in the diameter up to 4.9 μm. The solvent composition and monomer concentration greatly affected the polymerization behavior. Under appropriate conditions, monodisperse PMMA particles in the diameter up to 8.9 μm was prepared from 4.6 μm-sized seed particles. The seed dispersion polymerization of styrene in the presence of the seed particles produced monodisperse PMMA-polystyrene particles in the micron range. The particles were supposed to have a structure consisting of PMMA-core and polystyrene-shell from ESCA analysis.

INTRODUCTION

Micron-size monodisperse polymer particles have found wide applications in technical and biomedical fields. For preparation of such polymer particles, dispersion polymerization in polar media has been often used since the process is very simple without tedious operations, Especially, the dispersion of styrene in polar media was extensively studied to control the size and size distribution of the particles [1-6]. Monodisperse polystyrene particles with diameter up to 8 μm were prepared under appropriate reaction conditions [7].

It is necessary to find the suitable reaction conditions for each polymer [8-17] for preparation of micron-size uniform particles of other polymers by dispersion polymerization. There were several conditions reported for preparation of the monodisperse poly(methyl methacrylate) (PMMA) particles [1, 8-13]. Our previous paper [10] showed that such particles were obtained by using poly(N-vinyl-pyrrolidone) as stabilizer in a mixture of methanol and ethylene glycol. The selection of the mixed ratio of the solvents was very important for the achievement of the monodispersity. The monodisperse PMMA particles were also obtained by the dispersion copolymerization of MMA with a very small amount of a hydrophilic styryl-type poly(2-oxazoline) macromonomer in an aqueous methanol [12, 13]. In the dispersion polymerization system, the maximum size of monodisperse PMMA particles shown in photograph of scanning electron microscopy (SEM) was 4 μm [1, 8]. In the case of the production of larger PMMA particles by the dispersion polymerization technique, the size distribution was broader.

Seed emulsion polymerizations are widely employed for functionalizations of polymer latex [18]. However, since the added monomer amount to maintain the monodispersity of the seed particles is limited, this method is not suitable to increase the size of monodisperse particles. On the other hand, seed dispersion polymerization has be scarcely investigated; Okubo *et al.* reported that the seed dispersion polymerization of butyl methacrylate was carried out in the presence of uniform polystyrene particles (2 μm), which involved by-production of small particles (200 nm) [19]. The amount of butyl methacrylate was half as large as that of the polystyrene seed particles, therefore, the particle size after the seed polymerization was only a little larger than that of the seed particles. In the present paper, the seed dispersion polymerization using monodisperse PMMA seed particles has been examined. Under appropriate conditions, production of monodisperse PMMA particles up to 9 μm was achieved.

EXPERIMENTAL

Materials

Poly(methacrylic acid) (PMAA, Jurymer AC30H) was supplied by Nihon Junyaku Ltd. Other reagents and solvents were purchased from Wako Pure Chemical Industry Ltd., and used without further purification.

Preparation of PMMA Seed Particles

20 g of MMA, 20 g of 20% aqueous solution of PMAA, 0.20 g of AIBN, 64 g of methanol, and 16 g of water were weighted in a 300 mL glass bottle and the mixture was deoxygenated by bubbling nitrogen. Then, the bottle was placed on the shelf which was shaken at 160 times per minute in a water bath at 60°C for 10 hours. The resulting dispersion was used for the seed dispersion polymerization as it is.

Seed Dispersion Polymerization of MMA in the Presence of PMMA Seed Particles

A typical run was as follows (entry 2 in Table 1). A mixture of 20 g of MMA, 17.2 g of the dispersion of the seed particles, 10 g of 20% aqueous solution of PMAA, 0.20 g of AIBN, 64 g of methanol, and 16 g of water were weighted and deoxygenated by bubbling nitrogen. The bottle was shaken 160 times per minute in a water bath at 60°C for 10 hours. After the seed polymerization, the reaction mixture was subjected to centrifugation of the dispersion. The resulting particles were subjected twice to the resuspension in methanol and the successive centrifugation.

Seed Dispersion Polymerization of Styrene in the Presence of PMMA Seed particles

A typical run was as follows (run of Figure 5(A)). A mixture of 10.0 g of styrene, 8.6 g of the dispersion of the seed particles, 10 g of 20 % aqueous solution of PMAA, 0.10 g of AIBN, and 80 g of methanol were weighted and deoxygenated by bubbling nitrogen. The bottle was shaken 160 times per minute in a water bath at 60°C for 10 hours.

Measurements

Scanning electron microscopic (SEM) analysis was carried out by a JEOL JSM-T330 apparatus. Nominal circle diameter was determined by Nippon Avionics TV image processor EXCEL TVIP-4100 from SEM photographs. In each sample, the size of 200-300 particles was measured to calculate the size, size distribution,

and coefficient of variation of particles. Surface analysis by electron spectroscopy for chemical application (ESCA) was carried out with a Perkin Elmer X-ray photoelectron spectroscopy 5500-Series apparatus.

RESULTS AND DISCUSSION

Seed Dispersion Polymerization of MMA in the Presence of PMMA Seed Particles

PMMA seed particles were prepared by the dispersion polymerization using poly(methacrylic acid) stabilizer (PMAA, Mw = $5x10^4$) in an aqueous methanol at 60°C for 10 hours. The resulting particles were analyzed by SEM. In this study, size distribution (Dw/Dn) and variation of coefficient (Cv) were used as an index of dispersity. The seed particles were quantitatively obtained. SEM analysis showed the formation of relatively monodisperse PMMA particles (Dn = 2.49 μm; Dw = 2.58 μm; Dw/Dn = 1.04; Cv = 11.0%) (Figure 1(A)). In this study, the seed dispersion was used as obtained without isolation.

Seed dispersion polymerization was carried out by changing the amount of the added PMMA dispersion, *i.e.*, the weight ratio between the added monomer and the seed particles. Polymerization results were shown in Table 1. In all cases, the added monomer was quantitatively consumed. The diameter factors calculated from the weight ratio of MMA and the seed particles on the basis of the seed particles are 1.5, 2.0, 2.5, and 3.0 in four entries of Table 1. When the ratio between the added monomer and the seed particles was less than 7, the monodisperse PMMA particles were obtained (Figure 1(B) and (C)). In the polymerization with the ratio of 14.6, the size distribution became a little broader (Figure 1 (D)). The polymerization in the ratio of 26.0 afforded polydisperse particles (Figure 1(E)).

Figure 2 shows relationships between the weight ratio of the total monomer to the seed particle and volume of the resulting particles. In the low range of the ratio (less than 8), the particle volume linearly increased and was very close to the calculated value. On the other hand, the volume was smaller than the calculated value in the higher ratio. From these data, it was found that the new particles were formed during the seed polymerization in the high range of the ratio.

Next, the seed dispersion polymerization of MMA was performed using monodisperse PMMA particles in the diameter of 4.88 μm (entry 2 in Table 1) as seed particles under the similar reaction conditions of Table 1 in the diameter factor from 1.5 to 3.0. In all runs, monodisperse PMMA particles were not obtained; the formation of new small particles was observed.

TABLE 1. Seed Dispersion Polymerization of MMA in the Presence of Monodisperse PMMA Particles of Diameter in 2.49 μm[a]

	Seed Polymerization				Particles				
Entry	Amount of Seed Dispersion[b] (g)	MMA/Seed Particles[c]	MMA Conc.[d] (%)	Methanol/Water[c]	Dn[e] (μm)	Dn[f] (μm)	Dw[f] (μm)	Dw/Dn[f]	Cv[f,g] (%)
1	50.6	2.4	12.4	2.4	3.74	3.67	3.78	1.03	9.6
2	17.2	7.0	15.7	2.6	4.98	4.88	4.98	1.02	8.0
3	8.2	14.6	16.9	2.6	6.23	5.65	6.17	1.09	22.4
4	4.6	26.0	17.4	2.6	7.47	5.72	7.07	1.24	32.9

[a] Seed dispersion polymerization of MMA (20 g) was performed using PMAA stabilizer (2.0 g) in the presence of PMMA seed particles (Dn = 2.49 μm; Dw = 2.58 μm; Dw/Dn = 1.04; Cv = 11.0 %) by AIBN initiator (0.20 g) in an aqueous methanol at 60 ℃ for 10 h.

[b] Weight ratio of PMMA seed particles in the dispersion = 16.6 wt%.

[c] Weight ratio.

[d] Weight % based on the total.

[e] Calculalated from the weight ratio between MMA and seed particles.

[f] Determined by SEM.

[g] Coefficient of variation of number-average size.

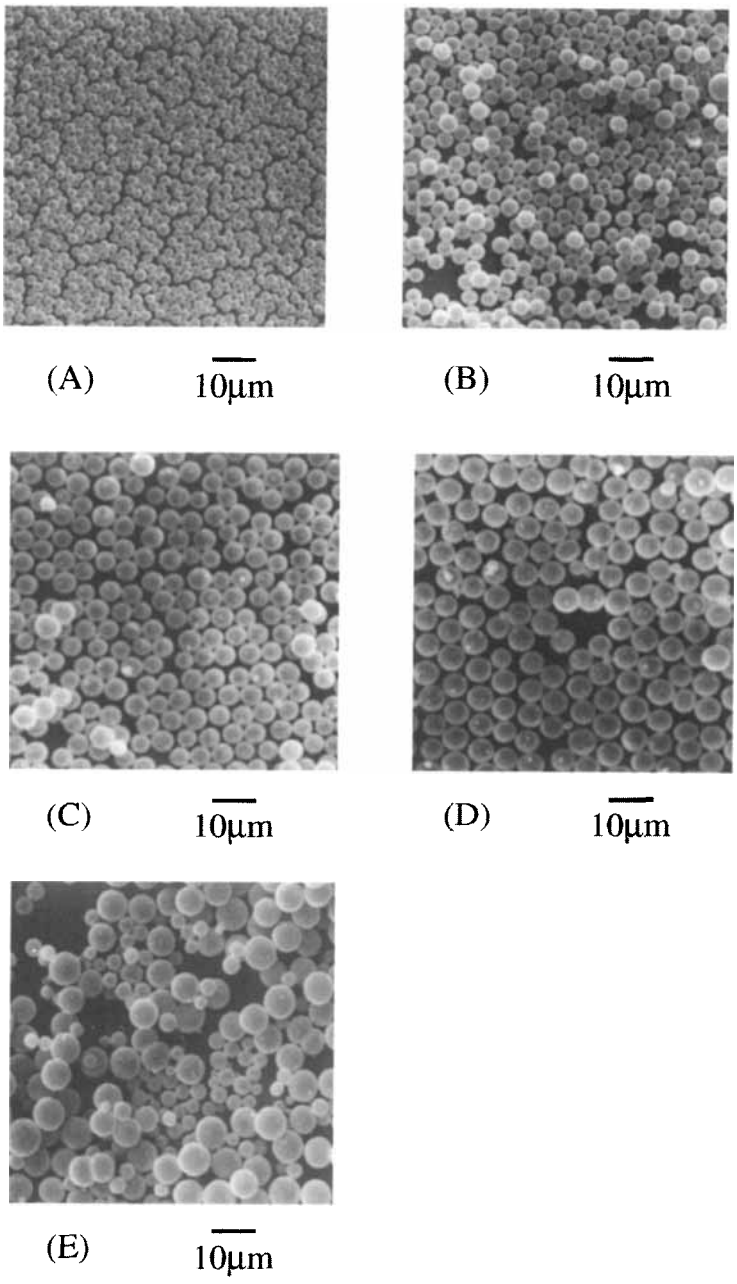

Figure 1. SEM photographs of PMMA particles obtained by seed dispersion polymerization using 2.49 μm-sized seed particles in the different feed weight ratios: (A) seed particles; (B) MMA/seed particles = 2.4; (C) 7.0; (D) 14.6; (E) 26.0.

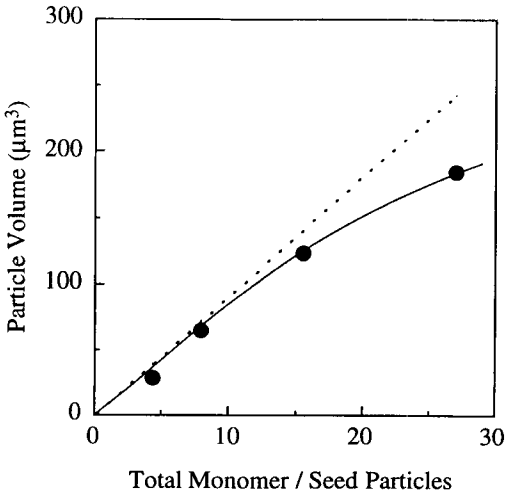

Figure 2. Relationships between the weight ratio of total monomer to the seed particle and particle volume.

In order to produce monodisperse PMMA particles by the seed polymerization using PMMA seed particles in the diameter of ca. 5 μm, the polymerization conditions to achieve the monodispersity of the particles have been screened. First, the solvent composition (mixed ratio of methanol and water) was examined (Table 2). The ratio of the added monomer to the seed particles was fixed as 7.0. The monodispersity was not achieved in under the conditions of the ratio of methanol/water of 2.7 (entry 1). Then, the polymerization in the larger ratio of methanol/water was performed. The polymerization in the ratio of 3.3 produced relatively monodisperse PMMA particles (entry 2), although there were a small amount of small new particles. In case of the ratio of 4.2, not only new small particles but also fused doublet and triplet particles were formed.

The effect of the monomer concentration was examined under the conditions of the methanol/water ratio of 4.2 (Table 3). Entry 1 in Table 3 (Figure 3(A)) was the same run of entry 3 in Table 2. The polymerization in the monomer concentration of 12.8 % produced relatively monodisperse particles (Figure 3(B)). The lower monomer concentration caused the production of much amount of new small particles (Figure 3(C)). These data indicate that the selection of the mixed ratio between methanol and water and of the monomer concentration was very important to produce monodisperse PMMA particles in the diameter of more than 5 μm.

TABLE 2. Effect of Solvent Composition in the Seed Dispersion Polymerization of MMA in the Presence of Monodisperse PMMA Particles of Diameter in 4.59 μm[a]

		Particles					
Entry	Methanol/Water[b]	Dispersity[c]	Dn[d] (μm)	Dn[e] (μm)	Dw[e] (μm)	Dw/Dn[e]	Cv[e,f] (%)
1	2.7	Polydisperse					
2	3.3	Relatively Monodisperse	9.38	9.40	9.86	1.049	16.6
3	4.2	Polydisperse					

[a] Seed dispersion polymerization of MMA (20 g; 15.9 wt% based on total; MMA/PMMA seed particles = 7.0) was performed in the presence of PMAA stabilizer (2.0 g) using PMMA seed particle dispersion (15.9 g; weight ratio of PMMA seed particles in the dispersion = 17.9 wt%; Dn = 4.59 μm; Dw = 4.69 μm; Dw/Dn = 1.021; Cv = 8.3 %) by AIBN initiator (0.20 g) in an aqueous methanol (100.7 g) at 60 ℃ for 10 h.

[b] Weight ratio.

[c] Observed by SEM.

[d] Calculalated from the weight ratio between MMA and seed particles.

[e] Determined by SEM.

[f] Coefficient of variation of number- average size.

TABLE 3. Effect of Monomer Concentration in the Seed Dispersion Polymerization of MMA in the Presence of Monodisperse PMMA Particles of Diameter in 4.59 μm[a]

Entry	MMA Conc.[b] (%)	Amount of Dispersion[c] (g)	MMA (g)	AIBN (g)	Particles					
					Dispersity[d]	Dn[e] (μm)	Dn[f] (μm)	Dw[f] (μm)	Dw/Dn[f]	Cv[f,g] (%)
1	15.9	15.9	20	0.20	Polydisperse					
2	12.8	11.9	15	0.15	Relatively Monodisperse	9.18	9.35	9.74	1.043	15.1
3	9.3	8.0	10	0.10	Polydisperse					

[a] Seed dispersion polymerization of MMA (MMA/PMMA seed particles = 7.0) was performed in the presence of PMAA stabilizer (2.0 g) using PMMA seed particle dispersion (Dn = 4.59 μm; Dw = 4.69 μm; Dw/Dn = 1.021 ; Cv = 8.3 %) by AIBN initiator in an aqueous methanol (methanol/water = ca. 4.2) at 60 ℃ for 10 h.

[b] Based on total.

[c] Weight ratio of PMMA seed particles in the dispersion = 17.9 wt%.

[d] Observed by SEM.

[e] Calculalated from the weight ratio between MMA and seed particles.

[f] Determined by SEM.

[g] Coefficient of variation of number-average size.

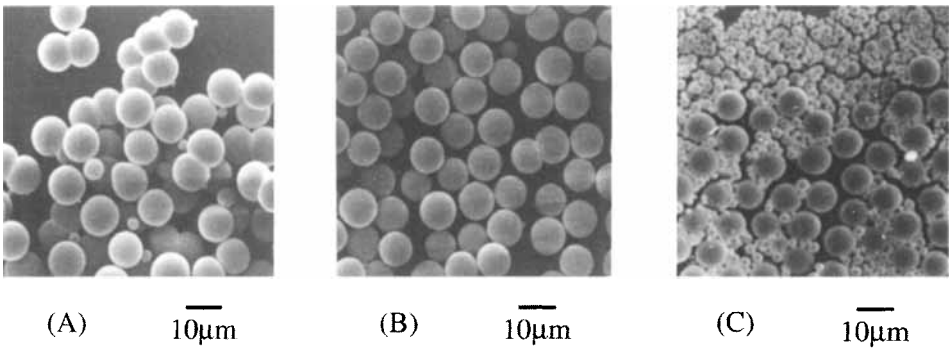

Figure 3. SEM photographs of PMMA particles obtained by seed dispersion polymerization using 4.59 μm-sized seed particles in the different MMA concentrations: (A) 15.9; (B) 12.8; (C) 9.3.

Considering the above data, the seed dispersion polymerization of MMA in the presence of PMMA seed particles having the diameter of ca. 5 μm was carried out in the high region of the methanol/water ratio (about 3.5) (Table 4). The diameter factors calculated from the weight ratio of MMA and the seed particles on the basis of the seed particles are 1.5, 1.6, 1.7, and 2.0 in four entries of Table 4. The quantitative consumption of the added monomer was confirmed. Figure 4 shows SEM photographs of the resulting PMMA particles. In all cases, relatively monodisperse PMMA particles were obtained, although a little amount of small particles were also formed. The diameter of the resulting particles was a little smaller than the calculated value, probably owing to the by-production of the small particles. By choosing the appropriate reaction conditions, the production of monodisperse PMMA particles in the diameter of ca. 9 μm was achieved (entry 4). When the feed ratio was beyond 2, the monodisperse particles were not obtained (data not shown).

Seed Dispersion Polymerization of Styrene in the Presence of PMMA Seed Particles

Core-shell type particles are of great interest in industrial fields. As a possible application, the seed dispersion polymerization of styrene was performed in the presence of monodisperse PMMA particles (Dn = 2.58 μm; Dw = 2.67 μm; Dw/Dn = 1.04; Cv = 10.7%). When the feed ratio of styrene to the seed particles was 2.4, monodisperse particles (Dn = 3.78 μm; Dw = 3.90 μm; Dw/Dn = 1.04; Cv

TABLE 4. Seed Dispersion Polymerization of MMA in the Presence of Monodisperse PMMA Particles of Diameter in 4.60 μm[a]

	Seed Polymerization				Particles				
Entry	Amount of Seed Dispersion[b] (g)	MMA/Seed Particles[c]	MMA Conc.[d] (%)	Methanol/Water[c]	Dn[e] (μm)	Dn[f] (μm)	Dw[f] (μm)	Dw/Dn[f]	Cv[f,g] (%)
1	46.9	2.4	12.7	3.4	6.90	6.64	6.74	1.02	8.1
2	36.0	3.1	13.7	3.5	7.36	6.91	7.12	1.03	12.3
3	28.5	3.9	14.4	3.5	7.82	7.57	7.66	1.01	6.3
4	16.0	7.0	15.9	3.7	9.20	8.94	9.04	1.01	6.3

[a] Seed dispersion polymerization of MMA (20 g) was performed using PMAA stabilizer (2.0 g) in the presence of PMMA seed particles (Dn = 4.60 μm; Dw = 4.70 μm; Dw/Dn = 1.02; Cv = 9.4 %) by AIBN initiator (0.20 g) in an aqueous methanol at 60 ℃ for 10 h.

[b] Weight ratio of PMMA seed particles in the dispersion = 17.9 wt%.

[c] Weight ratio.

[d] Weight % based on total.

[e] Calculalated from the weight ratio between MMA and seed particles.

[f] Determined by SEM.

[g] Coefficient of variation of number-average size.

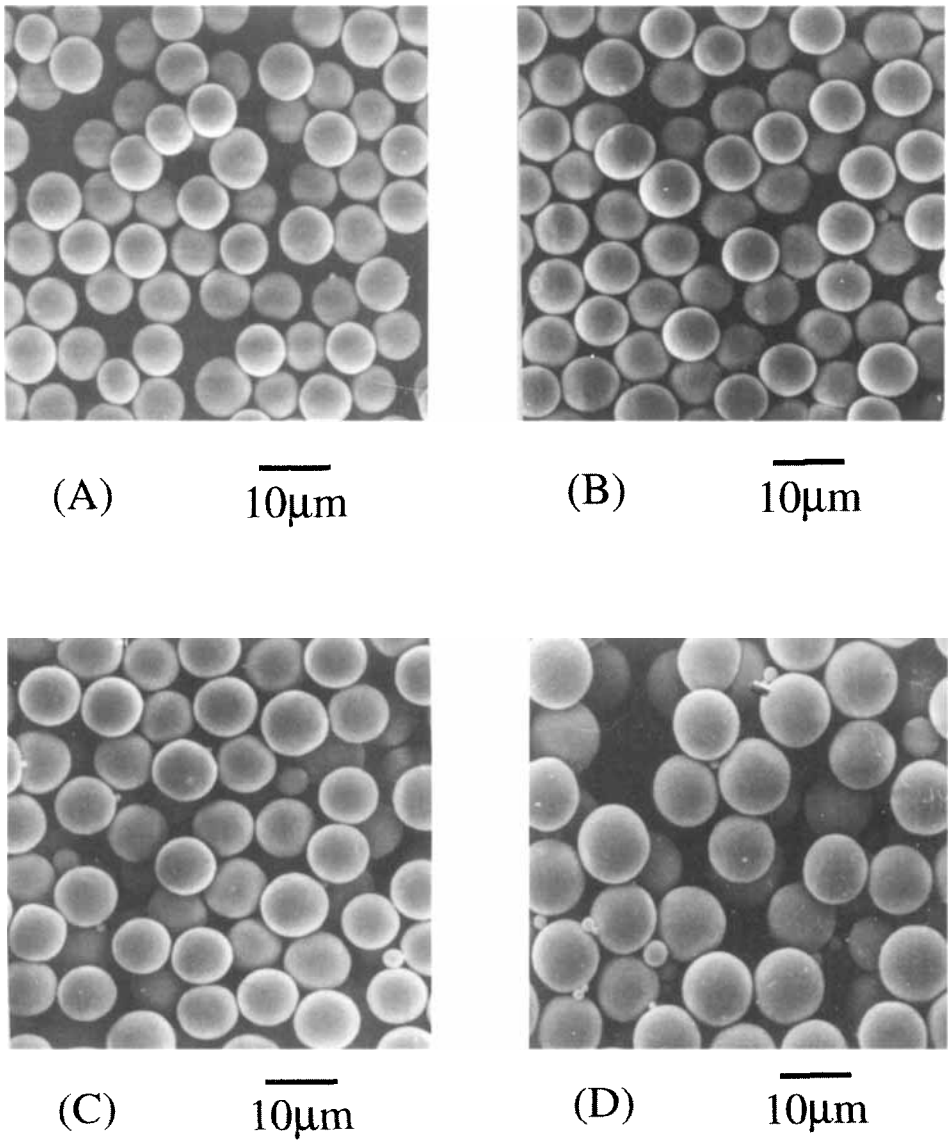

Figure 4. SEM photographs of PMMA particles obtained by seed dispersion polymerization using 4.60 μm-sized seed particles in the different feed weight ratios of MMA/seed particles: (A) 2.4; (B) 3.1; (C) 3.9; (D)7.0.

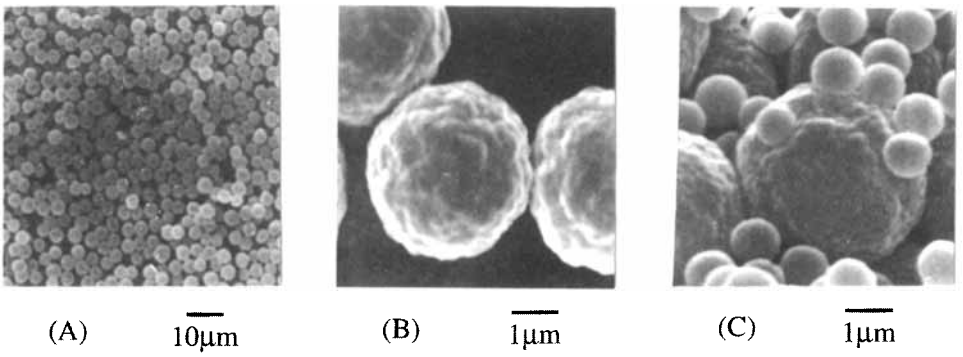

Figure 5. SEM photographs of PMMA-polystyrene composite particles obtained by seed dispersion polymerization of styrene using 2.58 μm-sized seed PMMA particles in the different weight feed ratios of styrene/seed particles: (A) and (B) 2.4; (C) 7.0.

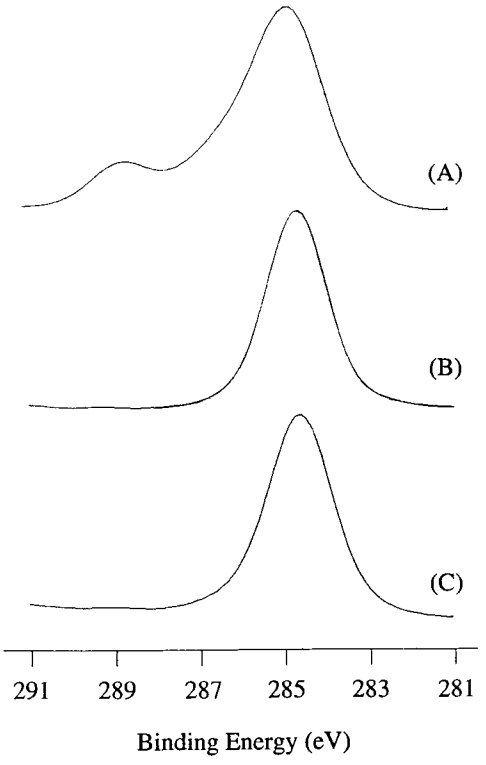

Figure 6. ESCA spectra of C1s region: (A) PMMA; (B) polystyrene; (C) PMMA-polystyrene core-shell type particles. The particles were obtained by seed dispersion polymerization of styrene using 2.58 μm-sized seed PMMA particles in the feed weight ratios of styrene/seed particles of 2.4.

= 9.5%) were formed (Figure 5(A)). The particle size was very close to the calculated value (3.87 μm). The magnified SEM photograph shows that the particle surface was somewhat uneven (Figure 5(B)). In case of the feed ratio of 7.0, the uneven particles as well as smaller particles with smooth surface were obtained (Figure 5(C)).

The surface analysis of the resulting particles was carried out by an electron spectroscopy for chemical application (ESCA) spectrometer. Generally, ESCA analysis gives information for a solid surface to a depth of 5-10 nm, and ESCA is a powerful tool for particle surface analysis of copolymers and polymer composites [20-22]. Figure 6 shows C1s peaks of PMMA, polystyrene, and the PMMA-polystyrene particles. The peak of the resulting particles was almost the same as that of polystyrene, suggesting that the present particles had a structure consisting of PMMA core and polystyrene shell.

CONCLUSION

Seed dispersion polymerization of MMA in the presence of monodisperse PMMA particles was carried out. From 2.5 μm-sized seed particles, monodisperse PMMA particles in the diameter up to 4.9 μm were obtained. The solvent composition and monomer concentration greatly affected the seed polymerization behavior. Under the appropriate conditions, production of relatively monodisperse PMMA particles in the diameter of 8.9 μm was achieved. This technique was applied to production of monodisperse core-shell type particles in the micron range. The particles were supposed to have a structure consisting of PMMA-core and polystyrene-shell from ESCA analysis.

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