

Morphology Control of Polymer Microspheres Containing Block Copolymers with Seed Polymerization

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Abstract

Microspheres based on binary polymer blend consisting of polystyrene (PSt), poly (methyl methacrylate) (PMMA), block copolymer comprising PSt and PMMA subunits, and ternary polymer blend consisting of PSt, PMMA, and block copolymer were fabricated by a solvent evaporation method, in which a polymer solution in dichloromethane was dispersed in water phase with the aid of a homogenizer to obtain an O/W emulsion followed by solvent evaporation with agitation to solidify the polymer. In the case of ternary blend, the effect of block copolymer content on the morphology of resulting spheres was investigated. Ternary blends afforded the bi-compartmental morphologies, the intermediate morphology between Janus and core-shell, which was confirmed by TEM observation. Seed polymerization of St or MMA was also carried out utilizing the resulting microspheres as seed particles in order to control the shape, and the surface morphology of particles. The particles with snowman-like morphology were obtained by seed polymerization of St using PSt/PMMA binary blend microspheres as seed particles. Surface roughness was controlled by the polymerization of MMA in the block copolymer seed, and that of St in the ternary blend seed.

Keywords

Microsphere, Morphology, Polymer Blend, Block Copolymer, Seed Polymerization

1. Introduction

Micron-sized, monodispersed polymer particles are of great interest for a wide variety of applications, for ex-

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ample, in the biomedical and environmental fields and in separation sciences [1]-[4]. In past decades, several polymerization techniques have been utilized to prepare polymeric particles with different size, such as emulsion polymerization, soap-free emulsion polymerization, suspension polymerization, dispersion polymerization and seeded emulsion polymerization. Among these, seeded emulsion polymerization is a good method for the preparation of particles with unique morphologies, such as multilayered core-shell [5]-[12], hemispheres [13] [14], and hollow structures [15] [16]. Okubo *et al.* reported seeded dispersion polymerization affording microspheres with specific shapes, such as snowman/confetti-like [17], hamburger-like [18], and disk-like [19].

It is also expected that particles based on block copolymers and polymer blends exhibit specific morphologies resulting from phase separations. In order to fabricate nanoparticles with inner micro-phase separated structure, Yabu *et al.* reported self-organized precipitation method [20] [21] in which a good solvent was evaporated from a block copolymer solution containing poor and good solvents. As for micron sized particles, the other type of solvent evaporation method has been used. In this method, a polymer solution is dispersed in an aqueous medium, and then the solvent is evaporated to solidify the polymer [22]-[24]. Phase-separation during the solvent evaporation afforded core-shell, and inverted core-shell, microdomain, hemisphere morphologies [22], and non-spherical shape of polystyrene/poly(methyl methacrylate) composite [23] [24].

In order to afford novel functionality to polymeric microspheres, it is important to control surface and inner morphology as well as the chemical structure, particle size and its distribution. In general block copolymers show nanometer sized microphase-separated structure, whereas simple polymer blends afford micrometer sized macrophase-separated structure. The addition of A-B block copolymer to the polymer blend consisting of homopolymers A and B decreases the domain size. Since phase separation in microspheres occurs in a limited space with large interface, it's possible to generate specific surface and inner morphology compared with bulk samples. Thus, it's important to understand the relationship between the fabrication conditions of microspheres and resulting morphology. In this paper, surface and inner morphologies were investigated for the microspheres based on the blends consisting of polystyrene (PSt), poly(methyl methacrylate) (PMMA) and PS-*b*-PMMA, and seed polymerizations of St and MMA were also conducted utilizing blend particles as the seed particles.

2. Experimental

2.1. Materials

Styrene (St), methyl methacrylate (MMA) (Wako Chemical, Japan), 1,1-diphenylethylene (DPE) (TCI, Japan) were purified by distillation under vacuum and stored in refrigerator before used. Tetrahydrofuran (Wako Chemical) was used as freshly distilled over sodium and benzophenone. *sec*-Butyl lithium (*sec*-BuLi) (1M in hexane) (Kanto Chemical, Japan), poly(vinyl alcohol) (PVA) (Kuraray, PVA224) as a stabilizer, 2,2'-azobis(isobutyronitrile) (AIBN) (TCI, Japan) as an initiator for radical seeded polymerization, sodium dodecyl sulfate (SDS) (TCI, Japan) as an emulsifier were used as received.

2.2. Anionic Polymerization of Styrene

After the evacuation followed with backfilling of nitrogen, 100-mL two-necked flask containing a magnetic stirrer bar was charged with dry THF (50 mL) under nitrogen atmosphere with a gas-tight syringe. After the temperature was down to -78°C with a dry ice/acetone bath, 0.96 mL (0.96 mmol) of *sec*-BuLi, and 10.1 mL of St (0.096 mol) were successively injected to the flask with gas-tight syringes. After 1 h, the reaction mixture was precipitated into methanol. The product was filtrated, washed with methanol and dried in vacuo. Yield: 9.28 g (93%).

2.3. Anionic Polymerization of Methyl Methacrylate

The procedure similar to that mentioned above was utilized. Under nitrogen atmosphere 30 mL of dry THF was added to the flask. After cooling to -78°C , 1 mL of *sec*-BuLi (1.00 mmol), and 10.6 mL of MMA (0.100 mol) were successively injected to the flask. After 1 h, the content of flask was poured into methanol. Yield: 7.36 g (73.6%).

2.4. Synthesis of Polystyrene-Block-Poly(methyl methacrylate)

Under nitrogen atmosphere 60 mL of dry THF was added to the flask. After cooling to -78°C , 1 mL of *sec*-BuLi

(1.00 mmol), and 11.5 mL of St (0.100 mol) were successively injected to the flask. After 1 h, 0.18 mL of DPE (1.00 mmol) was added dropwise. After stirring for 30 min, 10.6 mL of MMA (0.100 mol) was injected to the mixture. After 3 h, the reaction mixture was poured into methanol to precipitate the product. Yield: 18.0 g (88%).

2.5. Preparation of Seed Particles

Polymers (total: 1.5 g) were dissolved in 15 mL of dichloromethane. The solution was dispersed in 150 mL of H₂O containing 0.5 g of PVA with a homogenizer (X520, CAT Scientific, US) to obtain 5 - 15 μ m sized droplets. Dispersion was transferred to 300-mL beaker equipped with a mechanical stirrer, and the stirring was continued for 24 h to evaporate the solvent. The resulting particles were washed with distilled water with a centrifugation process.

2.6. Seed Polymerization of Styrene and Methyl Methacrylate

The dispersion of 0.5 g of seed particle in 40 mL of H₂O containing 0.24 g of PVA and 0.1 g of SDS 0.1 g was charged into the 100-mL three-necked flask with a mechanical stirrer. At 80 rpm, the emulsion of typically 0.5 g of monomer (St or MMA) and 40 mg of AIBN in 10 mL of H₂O containing 0.06 g of PVA and 0.02 g of SDS 0.02 g was dropwise added to the flask. After 24 h, the temperature increased to 70°C to initiate polymerization. After polymerization for 4 h, the product was washed with water and methanol, successively.

2.7. Characterization

Resulting PSt, PMMA and PS-*b*-PMMA were characterized with ¹H-NMR (ECX 300, JEOL). Molecular weight and polydispersity (PD) were estimated by gel permeation chromatography (GPC) equipped with JASCO 880-PUpump, a column packed with styrene-divinylbenzene gel beads [25], a JASCO UV-970 detector, and GPC. The surface feature of microspheres after evaporation of dichloromethane was characterized by scanning electron microscope (SEM) (JSM-6510, JEOL). Chloroform was used as an eluent, and the molecular weight was calibrated using polystyrene standards (SHODEX). The specimens for SEM observations were prepared by coating a thin gold film on the sample with an ion sputter coater (IB-3, Eiko Engineering). The morphologies inside the polymer particles were observed with transmission electron microscope (TEM) (JEM-2100, JEOL, Japan). The TEM specimens were prepared by cutting ultrathin films (ca. 70 nm in thickness) from particles embedded in epoxy resin (Epok 812) with an ultramicrotome (EM UC7, Leica) and setting them on the copper meshes. The PSt domain was stained by exposing the specimens to the vapor of an aqueous RuO₄ solution (0.5%) for 90 min in a sealed bottle at room temperature.

3. Results and Discussion

3.1. Preparation of Seed Particles

Table 1 shows number average molecular weights, M_n of PS, PMMA and PS-*b*-PMMA, obtained from anion polymerization. All the seed particles were fabricated using these three polymers. PVA concentration was adjusted to 0.6 wt% so that regular, spherical particles with a diameter of 3 - 10 μ m are obtained.

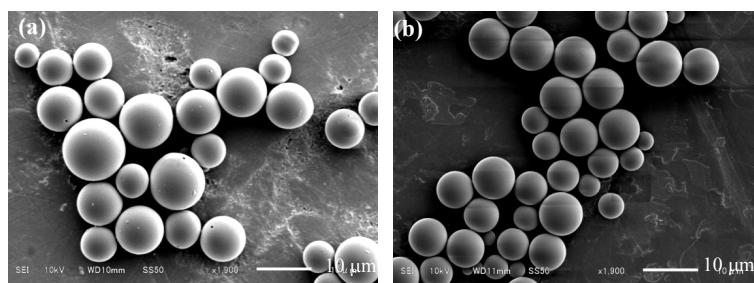
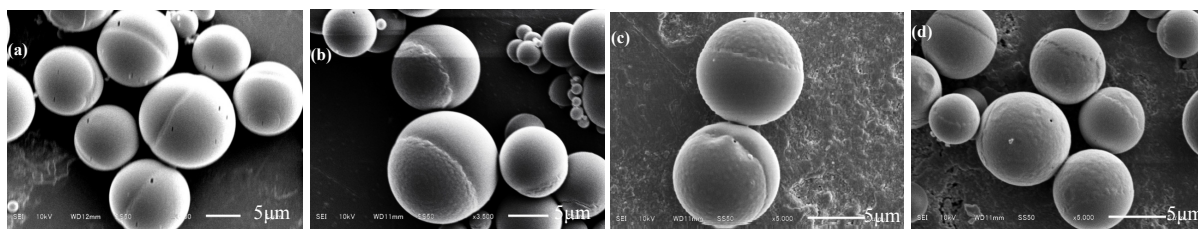
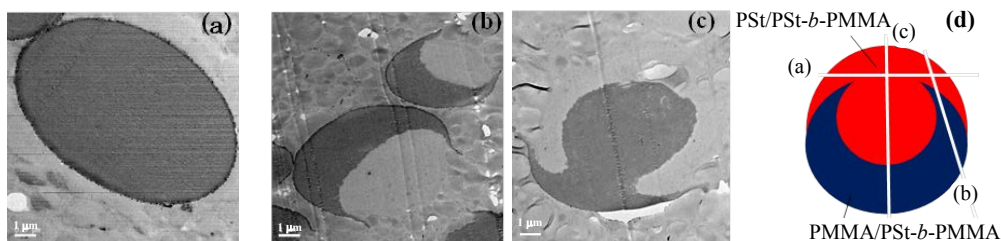
As shown in **Figure 1**, spherical and smooth particles were obtained both from PS/PMMA (PS/PMMA = 1:1) polymer blend (a), and block copolymer (b). PSt and PMMA homopolymers also afforded the smooth particles. As Ma et al. reported, a typical core-shell type morphology (PMMA; shell, PSt; core) is formed for PSt/PMMA blend when PVA was used as a stabilizer [22], and microphase separated structure for PSt-*b*-PMMA.

Microspheres based on the ternary blends consisting of PSt, PMMA, and PSt-*b*-PMMA were fabricated. As shown in **Figure 2**, particles with a boundary were obtained. The addition of 10 % of PSt-*b*-PMMA afforded particles with a line-shaped recess near the center of particles (**Figure 2(a)**). By the increase of the content of PSt-*b*-PMMA to 20%, particles with one smooth side and another rough side were obtained (**Figure 2(b)**). In the case of 30% and 40%, the portion of rough surface seemed to increase compared with 20% particles. **Figure 3** shows TEM images of particles based on ternary blend with 10% of block copolymer. As PSt is preferentially stained, black sites represent PSt rich domain. According to typical three types of images (**Figures 3(a)-(c)**), plausible morphology inside the particle is schematically represented in **Figure 3(d)**. It is found that the observed morphology is complex and intermediate between Janus and core-shell types.

Table 1. Molecular weights of PSt, PMMA, and PSt-*b*-PMMA.

Polymer	M_n^{PSt} ($\text{g}\cdot\text{mol}^{-1}$) ^a	M_n^{PMMA} ($\text{g}\cdot\text{mol}^{-1}$) ^a	PDI ^b	$f_{\text{PSt}}^{\text{c}}$
PSt	10,000	-	1.15	-
PMMA	-	12,000	1.25	-
PSt- <i>b</i> -PMMA	13,000	12,000	1.24	0.5

^aDetermined by GPC; ^bPolydispersity index determined by GPC; ^cVolume fraction of PSt.

**Figure 1.** SEM photographs of microspheres based on PSt/PMMA (1:1) blend (a) and PSt-*b*-PMMA (b) particles.**Figure 2.** SEM photographs of microspheres based on PSt/PSt-*b*-PMMA/PMMA ternary blend. (a) 0.45/0.1/0.45; (b) 0.4/0.2/0.4; (c) 0.35/0.3/0.35; (d) 0.3/0.4/0.3.**Figure 3.** TEM photographs of ultrathin cross sections of RuO₄-stained PSt/PSt-*b*-PMMA/PMMA composite particles prepared by solvent evaporation method (a)-(c). PSt/PSt-*b*-PMMA/PMMA = 0.45/0.1/0.45. Illustration (d) schematically indicates the plausible phase structure and the directions of slices.

Taking the low content and the comparable segment molecular masses of the block copolymer into consideration, macroscopic phase separation is expected. In general, it is supposed that A-B type block or graft copolymer acts as a compatibilizer for the homopolymers (A and B) blend. Block or graft copolymer decreases the free energy of interface between the polymer blend to facilitate the mixing of two phases. In this report, it is reasonable that PSt-*b*-PMMA exists both in PSt-rich and PMMA-rich phases, which decreases the difference of the surface energies at the interface between both oil and water phases (PSt-rich phase and PMMA-rich phase). As a result, a part of PSt-rich phase can locate at the interface with water to exhibit the intermediate morphology. In this morphology, PMMA unit of PSt-*b*-PMMA in PSt-rich domain is considered to be located at the interface between polymer and water phases to decrease the interfacial energy. Therefore, surface roughness observed in **Figures 2(b)-(d)** was probably derived from the aggregation of PSt-*b*-PMMA near the surface of PSt-rich domain.

3.2. Seed Polymerization

In a previous session, microspheres with various morphologies were obtained. Seed polymerizations of St and MMA were carried out in order to elucidate the effect of polymerization conditions on the final morphology.

At first, PS/PMMA blend particles were utilized as seeds. **Figure 4** shows SEM images of polymer particles after seed polymerization of MMA. When the amount of MMA was 10 or 100 wt% (a and b, respectively), no significant change was observed, and spherical particles with smooth surfaces were obtained. On the other hand, seed polymerization of 200 wt% of MMA afforded non-spherical particles with a bulge. From the optical microscope observation, particles swollen with MMA monomer show spherical shapes. Therefore it is considered that polymerization induced the irregular shape in the case of 200 wt% of MMA. As described in a previous session, seed particles have a core-shell morphology, hydrophilic PMMA shell, and hydrophobic PSt core. MMA monomer absorbed into seed particles is considered to be located in the shell part, and to be polymerized to form PMMA skin layer when the amount of MMA is not so high. With the increase of MMA monomer, the location of absorbed MMA extends over PSt core as well as PMMA shell. Polymerization of MMA in PSt phase induces the phase separation, resulting in the bulge.

Figure 5 shows SEM images of polymer particles after seed polymerization of St using PS/PMMA polymer blend seed particles. When 10 and 20 wt% of St was used, snowman-like particles were obtained (**Figure 5(a)** and **Figure 5(b)**). In the case of St, absorption of monomer also preferentially occurs at the PMMA shell, and stronger affinity between monomer and PSt core makes it possible to swell PSt core, resulting in protrusion of PSt/St mixture from the surface consisting of PMMA and St monomer. Indeed, **Figure 6** indicated that snowman-like droplets were formed before polymerization both for 10 and 100 wt% of St. When 10 and 20 wt% of St was used, the viscosity in the protruded mixture is much higher than that for 100 wt% of St. Higher viscosity leads to fixation of the morphologies before polymerization. On the other hand, the decrease of viscosity in 100 wt% mixture changes the shape from the swollen stage during polymerization (**Figure 5(c)**).

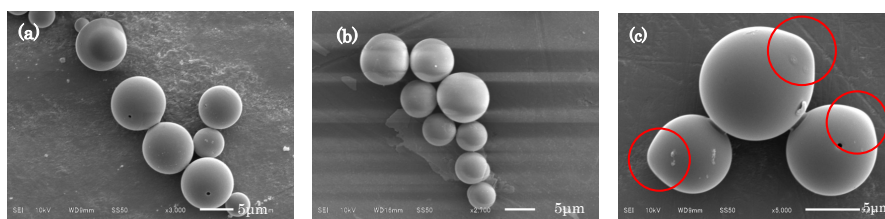


Figure 4. SEM photographs of polymer particles after seed polymerization of MMA using PS/PMMA seed particles. (a) MMA 10 wt%; (b) MMA 100 wt%; (c) MMA 200 wt%.

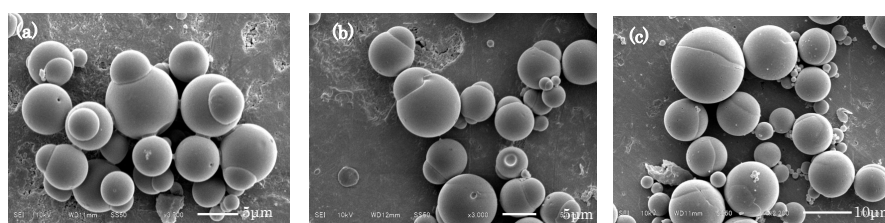


Figure 5. SEM photographs of polymer particles after seed polymerization of St using PS/PMMA seed particles. (a) St 10 wt%; (b) St 20 wt%; (c) St 100 wt%.

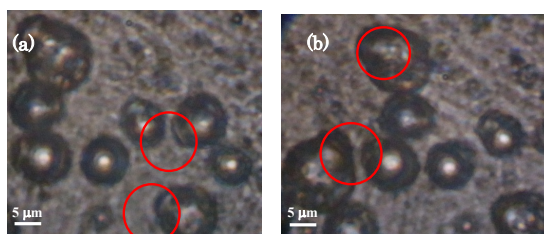


Figure 6. Optical microscope images of PS/PMMA seed particles after swelling with St. (a) St 10 wt%; (b) St 100 wt%.

Next, PSt-*b*-PMMA microspheres were used as seed particles, and final morphologies were observed after seed polymerization of MMA and St monomers. **Figure 7** shows SEM images of polymer particles after seed polymerization of MMA. Although the surface of seed particle is smooth (see **Figure 1(b)**), small protrusions with 100 nm size emerged after polymerization. At the stage of monomer absorption, surface is considered to consist of the mixture of MMA and the block copolymer. During polymerization, phase separation of resulting PMMA occurs near the surface to form the protrusions. With the increase of MMA amount, the surface tended to be covered with resulting PMMA more smoothly, and the surface roughness became discreet. Meanwhile, no significant morphology change was observed when St was used as a monomer as shown in **Figure 8**. Because of hydrophobicity of St, the absorbed monomer diffused toward the core direction compared with MMA. Polymerization of St and phase separation at the inside seems to have small effect on the surface morphology.

Finally seed polymerizations were carried out using ternary blend, and morphology changes were investigated. As discussed above, ternary blends consisting of PSt, PSt-*b*-PMMA, and PMMA show the unique bicompart-ment morphologies. **Figure 9** shows SEM images of polymer particles after seed polymerization of 10 wt% of MMA. Seed particles with 20 or 30 wt % of the block copolymer have rough surface of one side due to the ag-gregation of PSt-*b*-PMMA near the surface of PSt-rich domain. As shown in **Figure 9**, the surface became smoother after polymerization. This is probably due to the averaging effect by the formation of skin layer of hy-drophilic PMMA which is caused by the homogeneous distribution of MMA monomer on both surfaces. On the other hand, in the case of St (**Figure 10**), the surface of PMMA-rich phase became rougher with the increase of the block copolymer content (**Figure 10(b)** and **Figure 10(c)**). More St monomer is probably absorbed in PMMA-rich phase for the particles with the high content of PSt-*b*-PMMA, and polymerization induced phase separation inside the particle formed the protrusions.

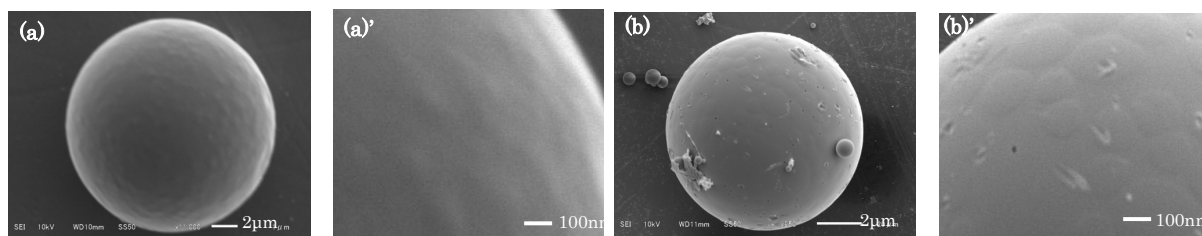


Figure 7. SEM photographs of polymer particles after seed polymerization of MMA using PSt-*b*-PMMA seed particles. (a) (a') MMA 10 wt%; (b) (b') MMA 20 wt%.

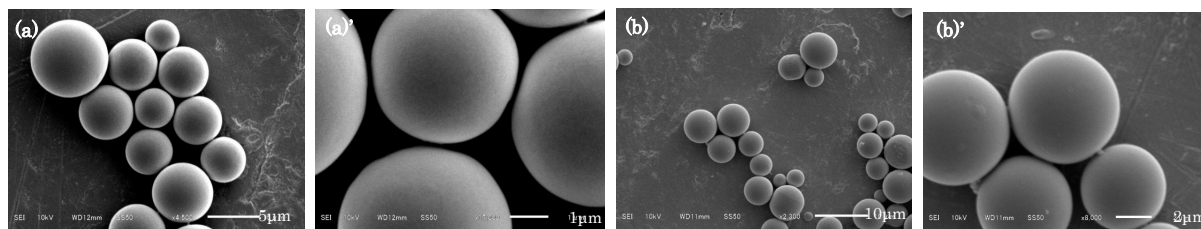


Figure 8. SEM photographs of polymer particles after seed polymerization of St using PSt-*b*-PMMA seed particles. (a) St 10 wt%; (b) St; 50 wt%.

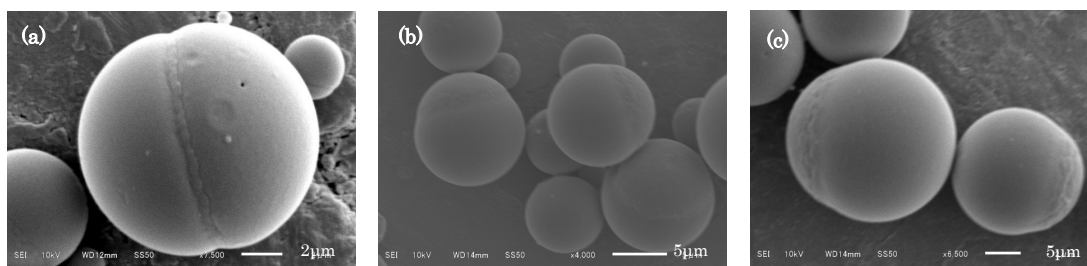


Figure 9. SEM photographs of polymer particles after seed polymerization of 10 wt % of MMA using PSt/PSt-*b*-PMMA/PMMA composite seed particles. PSt/PSt-*b*-PMMA/PMMA: (a) 0.45/0.1/0.45; (b) 0.4/0.2/0.4; (c) 0.35/0.3/0.35.

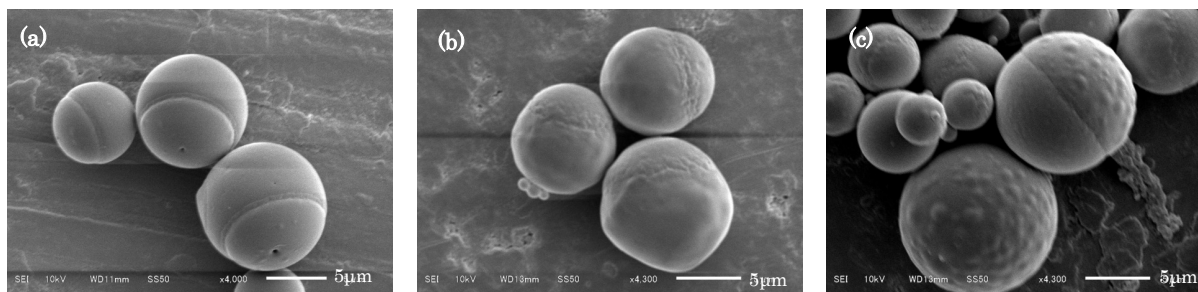


Figure 10. SEM photographs of polymer particles after seed polymerization of 10 wt % of St using PSt/PSt-*b*-PMMA/PMMA composite seed particles. PSt/PSt-*b*-PMMA/PMMA: (a) 0.45/0.1/0.45; (b) 0.4/0.2/0.4; (c) 0.35/0.3/0.35.

4. Conclusion

The microspheres with various types of surface and inside morphologies consisting of PSt/PMMA polymer blend, PSt-*b*-PMMA block copolymer and ternary (PSt/PSt-*b*-PMMA/PMMA) polymer blend were fabricated by a solvent evaporation method. Ternary blends afforded a unique morphology, intermediate between Janus and core-shell types. Bicompartiment morphology was confirmed by TEM observation. The difference of interfacial tensions of two polymers with aqueous phase decreased by the addition of the block copolymer. Seed polymerizations of St and MMA were also conducted, and the morphologies change was investigated. The particles with snowman-like morphology were obtained by seed polymerization of St using PSt/PMMA binary blend microspheres as seed particles. Some seed polymerizations also controlled the surface roughness, *i.e.* polymerization of MMA in the block copolymer seed, and that of St in the ternary blend seed. The microspheres with various surfaces and inside structure have potential applications in photonic and electronic fields.

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