

Morphology of polystyrene/polystyrene-*block*-poly(methyl methacrylate)/poly(methyl methacrylate) composite particles[☆]

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Abstract

Polystyrene/polystyrene-*block*-poly(methyl methacrylate)/poly(methyl methacrylate) (PS/PS-*b*-PMMA/PMMA) composite particles were prepared by releasing toluene from PS/PS-*b*-PMMA/PMMA/toluene droplets dispersed in a sodium dodecyl sulfate aqueous solution. The morphology of the composite particles was affected by release rate of toluene, the molecular weight of PS-*b*-PMMA, droplet size, and polymer composition. ‘Onion-like’ multilayered composite particles were prepared from toluene droplets of PS-*b*-PMMA and of PS/PS-*b*-PMMA/PMMA, in which the weights of PS and PMMA were the same. The layer thicknesses of the latter multilayered composite particles increased with an increase in the amount of the homopolymers. PS-*b*-PMMA/PS composite particles had a sea-islands structure, in which PMMA domains were dispersed in a PS matrix. On the other hand, PS-*b*-PMMA/PMMA composite particles had a cylinder-like structure consisting of a PMMA matrix and PS domains.

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1. Introduction

Composite polymer particles have been used in various applications such as impact modification, adhesives and coatings. The performance of composite polymer particles greatly depends on their morphology. Consequently, extensive research has been aimed at controlling particle morphology, resulting in the production of submicron-sized composite particles having a variety of different morphologies by seeded emulsion polymerization [1–9].

Recently, we have succeeded in the preparation of micron-sized, monodisperse, ‘onion-like’ multilayered poly(methyl methacrylate) (PMMA)/polystyrene (PS) composite particles. This was achieved by reconstruction of the morphology of PMMA-core/PS-shell composite particles, which were produced by seeded dispersion polymerization

(SDP) of styrene, with the solvent-absorbing/releasing method (SARM) [10]. In a previous article [11], PMMA-*g*-PS and/or PMMA-*b*-PS, which was formed during the SDP, played an important role as a compatibilizer in the formation of the multilayered structure. It is well known that a block copolymer, which consisted of their homopolymers, operates as a compatibilizer in polymer blend. Actually, there are many reports on microphase separation in polymer blend film containing block copolymer [12–14]. The experimental results and theoretical analysis indicate that the microphase separation of pure block copolymer (A-*b*-B) depends on the following three parameters: overall degree of polymerization (N); the Flory–Huggins interaction parameter (χ), which characterizes the repulsive interaction between the two blocks A and B; and the volume fraction of A phase. Masten et al. calculated the phase diagram for symmetric diblock copolymer melt [16]. For $\chi N < 10.5$, only a disordered melt is predicted. At larger values of χN , five ordered microstructures, which include lamellae, hexagonally packed cylinders, body-centered cubic spheres, close-packed spheres, and complex bicontinuous gyroid, are predicted to have regions of thermodynamically stable in

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the phase diagram. The experimental phase diagram of polyisoprene-*b*-PS blend film was obtained by Khandpur et al. [15]. Overall topology of the diagram is similar to the theoretical diagram and contains small regions of a second complex phase, perforated layers besides bicontinuous gyroid phase. However, to our knowledge, there are few reports about controlling the morphology of composite polymer particles by compatibilizer [17].

In this article, the effects of PS-*b*-PMMA on the morphology of PS/PS-*b*-PMMA/PMMA composite particles, especially, on the formation of the onion-like multilayered structure will be discussed. The composite particles were prepared by releasing toluene from polymers/toluene droplets dispersed in an aqueous medium.

2. Experimental

2.1. Materials

Styrene and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade of 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization. Three kinds of PS-*b*-PMMA (B5, B10, B17) having different molecular weights were purchased from Polymer Source Inc., Canada (see Table 1). Deionized water with a specific resistance of $5 \times 10^6 \Omega\text{cm}$ was distilled. The other materials were used as received from Nacalai Tesque Inc.

2.2. Preparation of PS/PS-*b*-PMMA/PMMA composite particles

PS and PMMA were prepared by solution polymerizations in toluene for 24 h, respectively, at 70 and 60 °C and at monomer conc. of 60 and 40 wt% and at AIBN conc. of 1.1 and 1.3 wt%. Number-average molecular weights (M_n)

Table 1
Molecular weights of PS, PMMA, and PS-*b*-PMMA

Ingredients	$M_{\text{PS}} (\times 10^4)^{\text{a}}$	$M_{\text{PMMA}} (\times 10^4)^{\text{b}}$	M_w/M_n
PS ^c	1.6	–	1.62
PMMA ^c	–	1.3	2.15
PS- <i>b</i> -PMMA ^d			
B5	5.0	5.4	1.04
B10	9.4	10.8	1.19
B17	17.0	16.8	1.10

Abbreviations: PS, polystyrene; PMMA, poly(methyl methacrylate); PS-*b*-PMMA, PS-*block*-PMMA.

^a Number-average molecular weight of PS or PS segment in PS-*b*-PMMA.

^b Number-average molecular weight of PMMA or PMMA segment in PS-*b*-PMMA.

^c Prepared by solution polymerizations in toluene with 2,2'-azobis(isobutyronitrile).

^d Purchased from Polymer Source Inc., Canada.

of both homopolymers were lower than any other M_n of each segment in PS-*b*-PMMA (see Table 1). A typical procedure for the preparation of composite particles is as follows. A homogeneous solution (1.1 g) of PS, PMMA, PS-*b*-PMMA, and toluene (polymers/toluene = 1/10, w/w) was mixed with 0.067 wt% SDS aqueous solution (30 g). The mixture was stirred vigorously using a NISSEI ABM-2 homogenizer at 2000 rpm for 2 min in a 50 ml glass cylindrical vessel. In order to change the release rate of toluene from the dispersion at room temperature, the dispersion was kept under stirring in a large Petri dish, a small Petri dish, a 300 ml beaker, a 100 ml beaker, and an uncovered glass cylindrical vessel whose evaporation areas between the dispersion and air were 125, 69, 43, 21, and 8 cm², respectively. The amount of residual toluene in the dispersions in the Petri dishes and the beakers were measured by gas chromatography every 10 and 20 min, respectively. In the case of the glass cylindrical vessel, the amount of toluene in the dispersion was measured every 1 h. Hereafter, the time taken for the amount of toluene to decrease to less than 1% of its original value is referred to as the 'release time'.

2.3. Observation of ultrathin cross-sections of particles

The dried particles were stained with RuO₄ vapor at room temperature for 30 min in the presence of 1% RuO₄ solution, and then dispersed in epoxy matrix, cured at room temperature for 24 h, and microtomed. The ultrathin cross-sections were observed with a Hitachi H-7500 transmission electron microscope (TEM).

2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data of PS and PMMA films, and PS-*b*-PMMA particles were obtained with Shimadzu ESCA-3400 electron spectrometer apparatus using magnesium K_α radiation (1253.6 eV) at a potential of 10 kV and an X-ray current of 20 mA. The pressure in the measurement chamber, in which the dried PS-*b*-PMMA particles were spread on an indium plate, was ca. 8.0×10^{-7} Pa. Before the measurement, each particle was centrifugally washed with water three times and dried under reduced pressure.

3. Results and discussion

Fig. 1 shows TEM photographs of ultrathin cross-sections of RuO₄-stained PS-*b*-PMMA (M_{PS} , 17.0×10^4 ; M_{PMMA} , 16.8×10^4) (B17) particles prepared by releasing toluene at different rates from B17/toluene droplets (1/10, w/w) in SDS aqueous medium. RuO₄ stains PS but not PMMA [18]. At high release rates shown in Fig. 1(a) and (b) small particles had an onion-like multilayered structure, but others were a disordered structure. On the other hand, at low

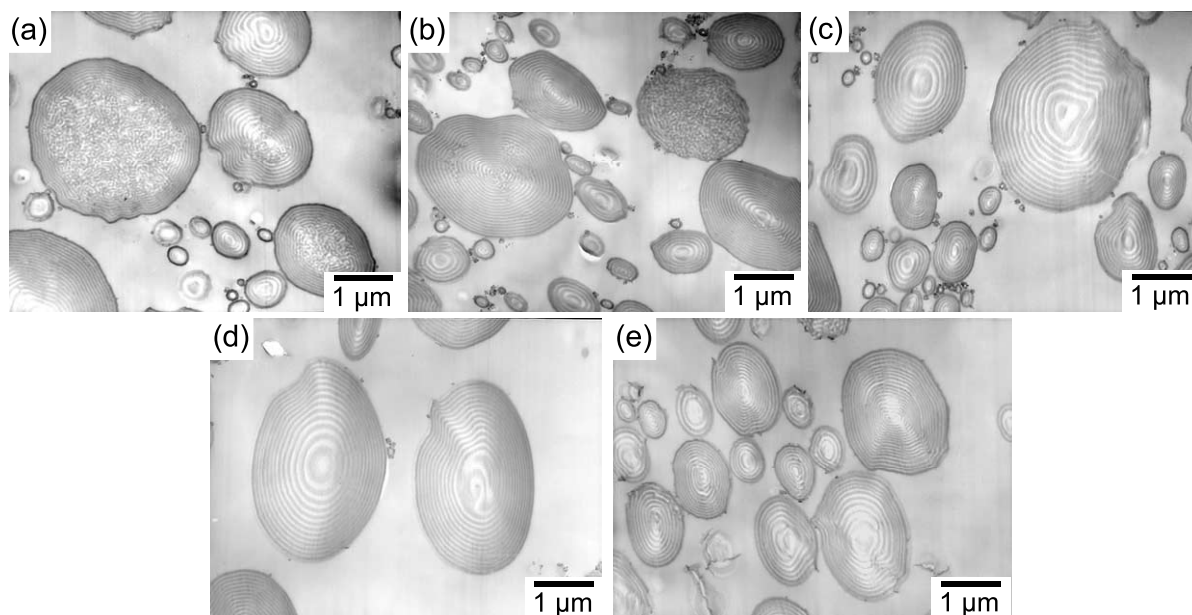


Fig. 1. Transmission electron microscope (TEM) photographs of ultrathin cross-sections of RuO_4 -stained polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) ($M_{\text{PS}}, 1.70 \times 10^5$; $M_{\text{PMMA}}, 1.68 \times 10^5$) particles prepared by releasing toluene from the polymer/toluene (1/10, w/w) droplets dispersed in sodium dodecyl sulfate (SDS) aqueous medium. Release times till the complete removal of toluene (min): (a) 20; (b) 30; (c) 60; (d) 180; (e) 1200.

release rates shown in Fig. 1(c)–(e), almost all particles had the onion-like multilayered structure. The lower the release rate was, the larger the ratio of the onion-like multilayered to the disordered structure was. It seems that some particles did not have enough time to form the multilayered structure, which should be thermodynamically stable, at high release rates. The following experiments were conducted at the lowest release rate (release time: 20 h).

Fig. 2 shows TEM photographs of ultrathin cross-sections of RuO_4 -stained PS-*b*-PMMA particles by releasing toluene from toluene droplets containing dissolved 10 wt% PS-*b*-PMMA having different molecular weights

dispersed in SDS aqueous medium. In the case of B17, the onion-like multilayered structure was observed as shown in Fig. 2(c) and (c'). On the other hand, as shown in Fig. 2(a') and (b') in the cases of B5 ($M_{\text{PS}}, 5.0 \times 10^4$; $M_{\text{PMMA}}, 5.4 \times 10^4$) and B10 ($M_{\text{PS}}, 9.4 \times 10^4$; $M_{\text{PMMA}}, 10.8 \times 10^4$), almost all particles had the disordered structure, although some small particles had the onion-like multilayered structure. These results suggest that the molecular weight of PS-*b*-PMMA and the droplet size are important factors for the formation of the multilayered structure.

Fig. 3 shows a C_{1s} XPS of the PS-*b*-PMMA particles having the highest molecular weight (B17). Before the

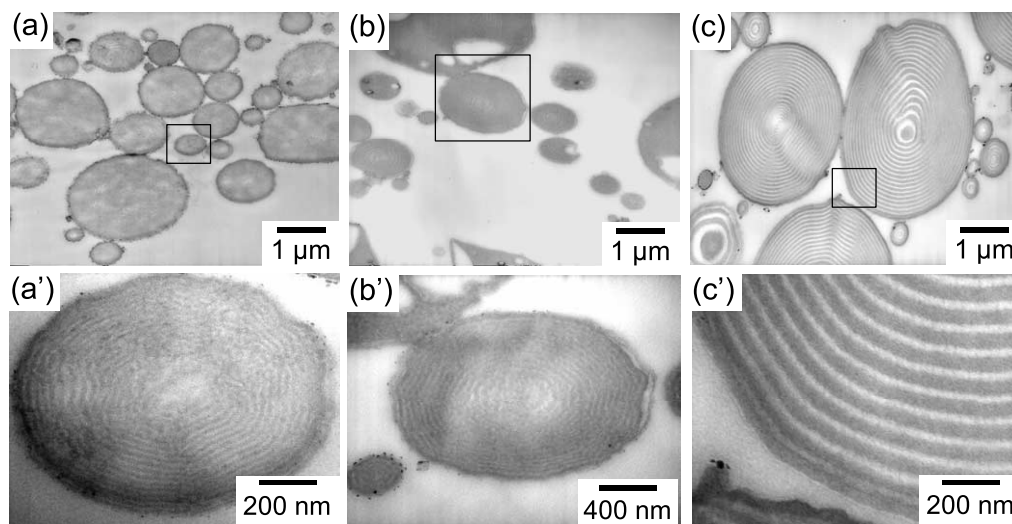


Fig. 2. TEM photographs of ultrathin cross-sections of RuO_4 -stained PS-*b*-PMMA particles prepared by releasing toluene from the polymer/toluene (1/10, w/w) droplets dispersed in SDS aqueous medium at the release time of 20 h. M_n of PS-*b*-PMMA ($\times 10^5$): (a) and (a') 1.04; (b) and (b') 2.02; (c) and (c') 3.38.

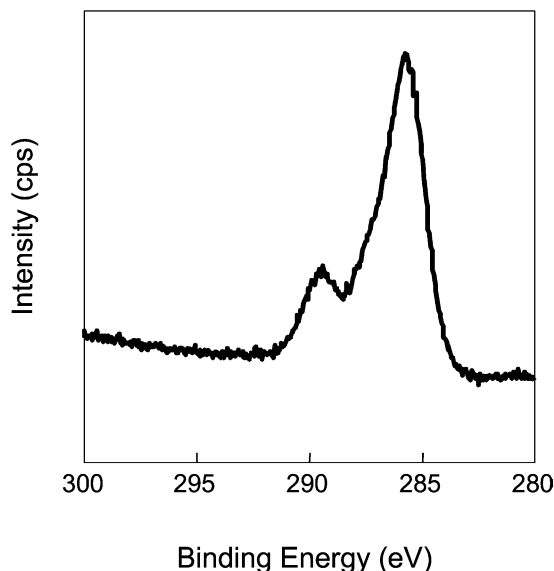


Fig. 3. C_{1s} X-ray photoelectron spectrum of the PS-*b*-PMMA (M_{PS} , 1.70×10^5 ; M_{PMMA} , 1.68×10^5) particles prepared by releasing toluene from the polymer/toluene droplets (1/10, w/w) dispersed in SDS aqueous medium.

measurement, the particles were centrifugally washed. In comparison with those [19] of PS and PMMA (data were omitted), the XPS spectrum of the B17 particles, which had a peak due to carbonyl groups of PMMA at ca. 289 eV, was similar to that of the PMMA. This shows PMMA occupied at the B17 particle surface, which would be thermodynamically stable in water.

The solubility limit of homopolymer in the microstructure of diblock copolymer has been treated previously by Meier [20], and phase behavior of the A-*b*-B/A system has

been theoretically and experimentally investigated by Noolandi et al. and Roe et al., respectively [21,22]. Their studies show that the length of the homopolymer needs to be of the same order of magnitude or smaller than the corresponding block length to be soluble in the microstructure of the block copolymer. The solubility limit decreases with increasing molecular weight of the homopolymer. On the basis of this idea, the thickness and the morphology of multilayered composite particles would be controllable by including homopolymer into block copolymer. The following experiments were conducted for PS-*b*-PMMA containing PS and/or PMMA having lower molecular weights than each segment in the PS-*b*-PMMA.

Fig. 4 shows TEM photographs of ultrathin cross-sections of RuO₄-stained PS-*b*-PMMA (B17)/PS (50/50–100/0, w/w) composite particles prepared by releasing toluene from polymers/toluene droplets (1/10, w/w) in SDS aqueous medium. At the B17/PS ratio of 80/20, the composite particles seem to have a cylinder-like structure (b) or a mixed microstructure (c) of cylinder-like (d) and bicontinuous gyroid (e). Forster et al. reported from additional results of small-angle X-ray and neutron scattering that similar TEM images as shown in Fig. 4(b)–(e) show the hexagonally packed cylinders and the bicontinuous gyroid structures [23]. At the ratio of 50/50 (f), the composite particles had a sea-island structure consisting of PS matrix and PMMA domains. The morphology of the composite particles was continuously changed from the multilayered to the sea-island structure with an increase in the PS content.

Fig. 5 shows TEM photographs of ultrathin cross-sections of RuO₄-stained B17/PMMA (100/0–50/50, w/w)

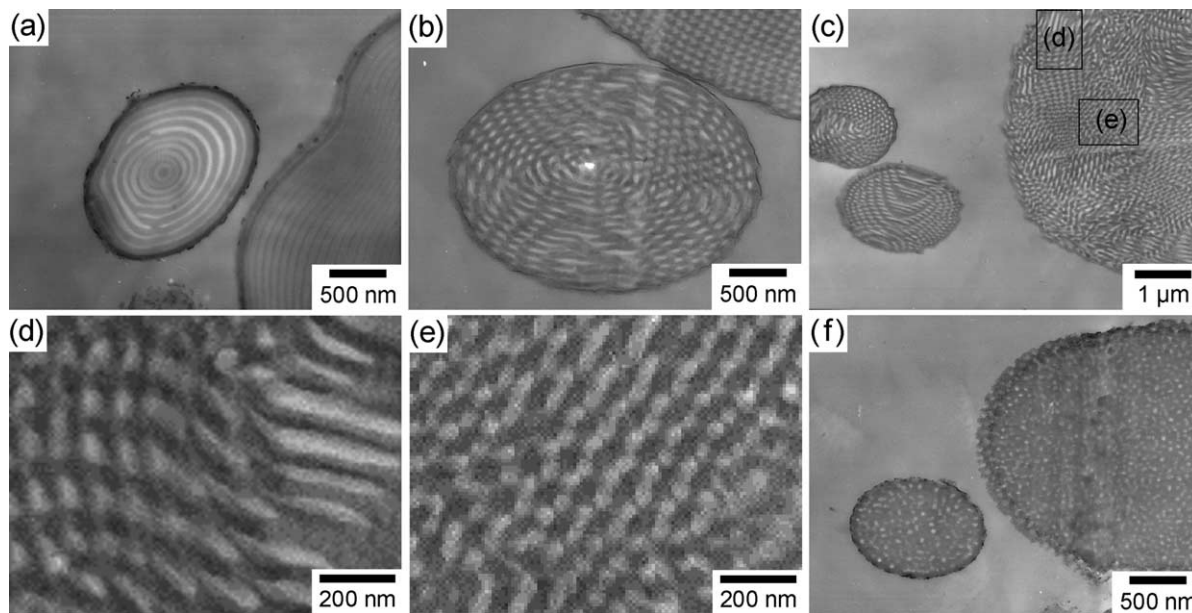


Fig. 4. TEM photographs of ultrathin cross-sections of RuO₄-stained PS-*b*-PMMA (M_{PS} , 1.70×10^5 ; M_{PMMA} , 1.68×10^5)/PS composite particles prepared by releasing toluene from the polymers/toluene (1/10, w/w) droplets dispersed in SDS aqueous medium at the release time of 20 h. PS-*b*-PMMA/PS (w/w): (a) 100/0; (b)–(e) 80/20; (f) 50/50.

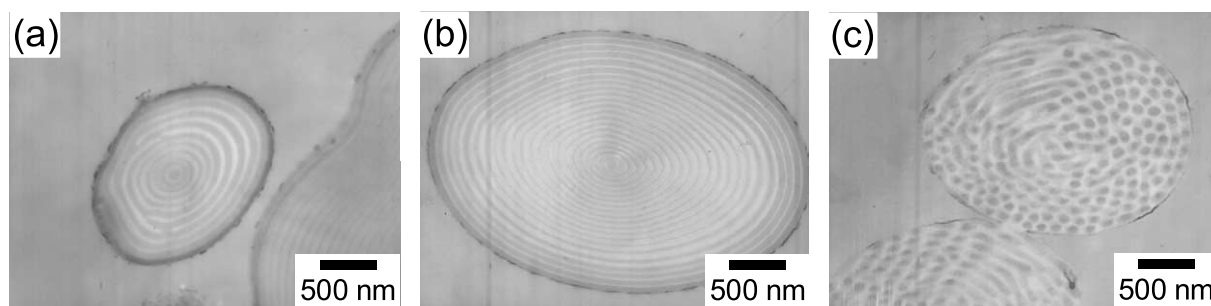


Fig. 5. TEM photographs of ultrathin cross-sections of RuO_4 -stained PS-*b*-PMMA ($M_{\text{PS}}, 1.70 \times 10^5$; $M_{\text{PMMA}}, 1.68 \times 10^5$)/PMMA composite particles prepared by releasing toluene from the polymers/toluene (1/10, w/w) droplets dispersed in SDS aqueous medium at the release time of 20 h. PS-*b*-PMMA/PMMA (w/w): (a) 100/0; (b) 80/20; (c) 50/50.

composite particles prepared by releasing toluene from polymers/toluene droplets (1/10, w/w). The morphology of the composite particles at the B17/PMMA ratio of 80/20 (b) had the multilayered structure similar to B17 particles (a). On the other hand, in the case of the ratio of 50/50 (c), the morphology of B17/PMMA particles seems to have a cylinder-like structure consisting of PMMA matrix and PS domains. These results suggest that the morphology of symmetrical A-*b*-B/A or A-*b*-B/B composite particles changes from the multilayered to the cylinder-like and subsequently to the sea-island structures with an increase in the A (or B) content. This is similar to that the morphology of the SARM-treated PMMA/PS composite particles, which had been produced by the SDP, depended on the polymer composition [24].

Fig. 6 shows TEM photographs of ultrathin cross-sections of RuO_4 -stained PS/B17/PMMA composite particles prepared by releasing toluene from the polymers/

toluene droplets (1/10, w/w). All the composite particles had the onion-like multilayered structure. However, as shown in Fig. 6(d) and (e) at low B17 contents of 20 and 10 wt%, the thickness of each layer was not homogeneous in the multilayered structures. The incompleteness seems to be based on that the amount of the PS-*b*-PMMA was not enough to form the complete onion-like multilayered structure. The thicknesses of the layers decreased with an increase in the amount of B17.

From these results, it is concluded that onion-like multilayered polymer particles can be prepared by releasing toluene from toluene droplets dissolving PS-*b*-PMMA or PS/PS-*b*-PMMA/PMMA dispersed in SDS aqueous solution under optimum conditions.

Acknowledgements

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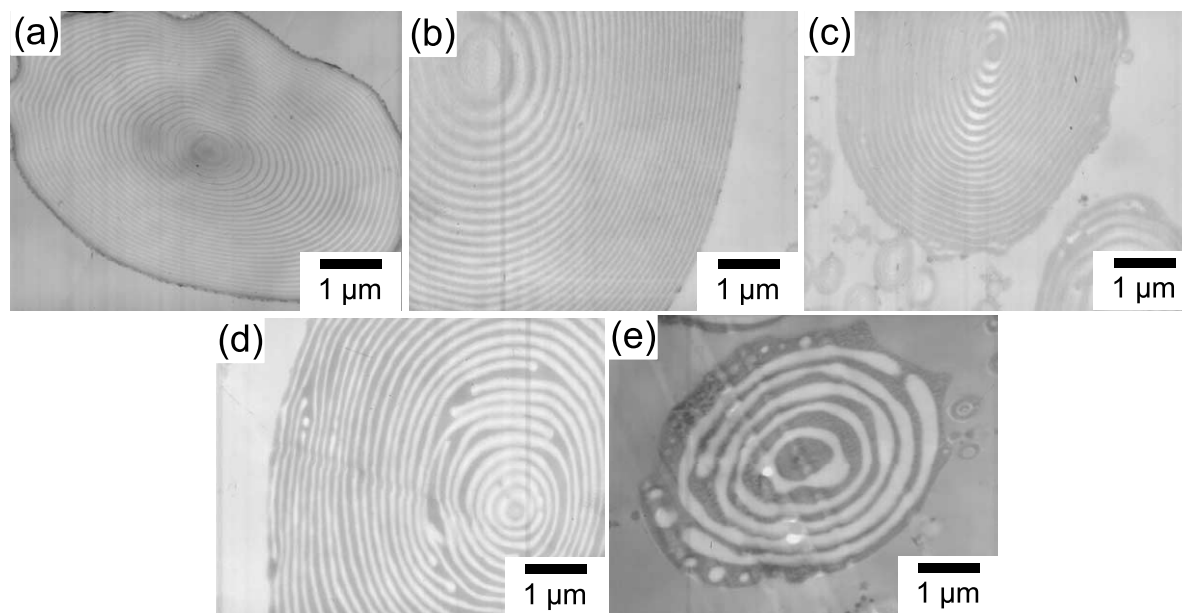


Fig. 6. TEM photographs of ultrathin cross-sections of RuO_4 -stained PS/PS-*b*-PMMA ($M_{\text{PS}}, 1.70 \times 10^5$; $M_{\text{PMMA}}, 1.68 \times 10^5$)/PMMA composite particles prepared by releasing toluene from the polymers/toluene (1/10, w/w) droplets dispersed in SDS aqueous medium at the release time of 20 h. PS/PS-*b*-PMMA/PMMA (w/w/w): (a) 0/100/0; (b) 25/50/25; (c) 35/30/35; (d) 40/20/40; (e) 45/10/45.

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