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ORIGINAL CONTRIBUTION

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Preparation of polystyrene/poly(methyl methacrylate) composite particles having a dent

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Abstract Nonspherical polystyrene (PS)/poly(methyl methacrylate) (PMMA) composite particles having a dent were prepared by releasing toluene from PS/PMMA/toluene droplets dispersed in a poly(vinyl alcohol) aqueous medium. An ex-centered PS-core/PMMA-shell morphology, in which a part of the PS core contacted with the aqueous medium and toluene partitioned more in the PS core than in the PMMA shell, was formed in the polymers/toluene droplet in the process of phase separation therein with releasing toluene. The volume of the dent became bigger with an increase in the PS content and in the toluene content partitioned in the PS core.

Keywords Phase separation · Hemispherical structure · Dent · Morphology · Particle/medium interface

Introduction

Composite polymer particles have been used in various applications such as impact modification, adhesives, and coatings. The performance of the composite polymer particles greatly depends on their morphology. Consequently, extensive research has been aimed at controlling the particle morphology and clarified that the morphology is affected by many factors [1–13]. Composite polymer particles are generally produced by seeded polymerization techniques, where a second-stage monomer is polymerized in the presence of seed polymer particles. In a general seeded dispersion polymerization (SDP), where most of the second-stage monomers exist in the medium, diffusion of polymer radicals generated in the medium into the seed particle is extremely slow because of high viscosity therein. Therefore, this technique can be used to produce the core/shell composite polymer particles, and actually ca. 2-μm-sized monodisperse composite polymer particles having chloromethyl groups [14] and vinyl groups [15, 16] locally in the surface layers were produced by SDP.

In a previous article, poly(methyl methacrylate) (PMMA)/polystyrene (PS) composite particles consisting of a PMMA-core and a PS-shell were produced by SDP of styrene with 1.91-μm-sized monodisperse PMMA seed particles [17]. When the PMMA/PS composite particles were swollen by toluene, in which both the polymers dissolved, and the toluene was slowly released therefrom by evaporation, "onion-like" alternately multilayered spherical PS/PMMA composite particles were prepared [18]. A small amount of PMMA-*graft*-PS and/or PMMA-*block*-PS, which were formed during the SDP, played an important role in forming the multilayered structure [19]. In our research, in order to examine the influence of the graft or block polymer, we

Table 1 Preparations of polystyrene (PS), poly(methyl methacrylate), styrene-1-pyrenylmethyl methacrylate copolymer (P(S-PM)), polychloromethylstyrene (PCMS) and styrene-chloromethylstyrene copolymer [P(S-CMS)] by solution polymerizations

Ingredients	PS[a]	PMMA[b]	P(S-PM)[a]	PCMS[a]	P(S-CMS)[a]
Styrene (g)	18	–	3	–	5.4
Methyl methacrylate (g)	–	13	–	–	–
1-Pyrenylmethyl methacrylate (mg)	–	–	15	–	–
Chloromethylstyrene (g)	–	–	–	18	0.6
Toluene (g)	12	19	2	12	4
2,2′-Azobis(isobutyronitrile) (mg)	54	400	10	54	18
M_w[c] (10^4 g/mol)	10	9.4	9.8	7.9	9.7
M_w/M_n[d]	1.7	1.9	1.6	2.0	1.6

[a] 60°C, 24 h, N_2

[b] 70°C, 24 h, N_2

[c] Weight-average molecular weight measured by gel permeation chromatography

[d] Number-average molecular weight measured by gel permeation chromatography

prepared PS/PMMA composite particles containing no such graft or block polymer by releasing the solvent from solvent droplets dissolving PS and PMMA, which were separately formed by solution polymerizations, dispersed in poly(vinyl alcohol) aqueous medium. When toluene was used as solvent, nonspherical PS/PMMA composite particles having a dent were obtained. Control of particle shape is one of the key factors for the functionalization of particles in the applications.

In this article, the morphology and the formation mechanism of such nonspherical PS/PMMA composite particles are discussed.

Experimental

Materials

Styrene and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) was purified by recrystallization. Reagent grade chloromethylstyrene (CMS) (Seimi Chemical Co. Ltd.), 1-pyrenylmethyl methacrylate (PM) (Funakoshi, Tokyo, Japan), and 4,4′-diisothiocyanatostilbene-2,2′-disulfonate (DIDS) (Funakoshi, Tokyo, Japan) were used as received. PVA (Gohsenol GH-17: degree of polymerization, 1,700; degree of saponification, 88%) was supplied by Nippon Synthetic Chemical, Osaka, Japan. Deionized water with a specific resistance of 5×10^6 Ω·cm was distilled. The other materials were used as received from Nacalai Tesque Inc., Kyoto, Japan.

Preparation of PS/PMMA composite particles

Polystyrene and PMMA were prepared by solution polymerizations under the conditions listed in Table 1. The homopolymers were precipitated from toluene solution into excess methanol, and dried in vacuum at room temperature. Homogeneous solutions (0.65 g) of the PS and the PMMA (polymer/solvent = 1/12, w/w) were separately mixed with 0.67 g/l PVA aqueous solution (15 g). The resultant mixtures were stirred vigorously using a NISSEI ABM-2 homogenizer at 2,000 rpm for 2 min in 50-ml-glass cylindrical vessels. The solvent was released by evaporation from the dispersions on stirring with a magnetic stirrer at room temperature for 24 h in the uncovered glass cylindrical vessels.

Observation of the composite polymer particles

The PS/PMMA composite particles dried at room temperature were observed with a Hitachi S-2460 scanning electron microscope (SEM). The internal morphology of the composite particles was observed as follows. The dried composite particles were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 aqueous solution, dispersed in an epoxy matrix, and the epoxy matrix was cured at room temperature for 24 h, and microtomed. The ultrathin cross sections were observed with a Hitachi H-7500 transmission electron microscope (TEM).

Phase diagram of the PS/PMMA/solvent systems

Various compositions of the PS/PMMA/ethylbenzene and PS/PMMA/chloroform (polymers/solvent = 1/7~1/11, w/w) solutions were poured into graduated cylinders. Then the solutions were left standing in the closed cylinders at room temperature for 2 weeks. When phase separation occurred and each solution separated into two layers, the total amounts and the weight ratios of PS and PMMA in the two layers were measured by gravimetry and ^{1}H NMR, respectively. The volume ratio of PS/PMMA/solvent in each layer was calculated from the amounts of the polymers and the volume of each layer, which was estimated from the graduation of the cylinder. It was difficult to measure the volume ratio in each layer near the cloud point, because the solutions did not separate clearly into two layers. In order to construct the phase diagrams near the cloud point, various volume ratios of PS/PMMA/ethylbenzene (0.02~0.05/0.02~0.07/0.91~0.94, v/v/v) or PS/PMMA/chloroform (0.02~0.11/0.01~0.08/0.86~0.94, v/v/v) solutions were observed with the naked eye, judging whether cloudy or clear.

Observation of phase separation in droplets with a confocal laser scanning microscope

The S-PM copolymer [P(S-PM)] was prepared by solution polymerization of styrene and a small amount of PM as fluorescent monomer under the conditions listed in Table 1. A homogeneous solution (0.65 g) of P(S-PM)/PMMA/toluene (1/9/120, w/w/w) was mixed with PVA aqueous solution with homogenizer. Toluene was released by evaporation from the dispersion, and the droplets were observed at different storage times with a confocal laser scanning microscope (CLSM).

X-ray photoelectron spectroscopy

Polychloromethylstyrene (PCMS) was formed by solution polymerization under the conditions listed in Table 1. PCMS particles were prepared by releasing toluene from PCMS (50 mg)/toluene (0.6 g) droplets dispersed in PVA aqueous medium. The PCMS particles (50 mg) were aminated with 13.3% CH_3NH_2 aqueous solution (15 g) at room temperature for 100 h. After the amination, the PCMS particles were centrifugally washed with distilled water and dried under reduced pressure. The X-ray photoelectron spectroscopy (XPS) data of the CH_3NH_2-modified PCMS particles were obtained with a Shimadzu ESCA-3400 electron spectrometer apparatus using magnesium K_α radiation (1,253.6 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 PCMS particles were spread on an indium plate, was ca. 8.0×10^{-7} Pa. Argon ion sputtering was conducted at 5.0×10^{-4} Pa for 120 s at an acceleration voltage of 2.0 kV and at an ion beam current of 20 mA.

Observation of CH_3NH_2-modified P(S-CMS)/PMMA composite particles after reaction with the fluorescence dye

The P(S-CMS)/PMMA composite particles were prepared in the same way as described above. Then the P(S-CMS)/PMMA composite particles (50 mg) were aminated with 13.3% CH_3NH_2 aqueous solution (15 g) at room temperature for 100 h. After the amination, the CH_3NH_2-modified P(S-CMS)/PMMA composite particles (50 mg) were centrifugally washed with water and dispersed in 0.67 g/l DIDS (fluorescence dye) aqueous solution (30 g) at room temperature for 100 h. The CH_3NH_2-modified P(S-CMS)/PMMA composite (50 mg) particles after reaction with DIDS were observed with the CLSM. As a blank test, the PS/PMMA composite particles having a dent were reacted with CH_3NH_2 and with DIDS and then observed with the CLSM in the same manner as described above.

Results and discussions

Figure 1 shows an optical micrograph (a) and an SEM photograph (b) of PS/PMMA (1/1, w/w) composite particles prepared by releasing toluene from the polymers/toluene (1/12, w/w) droplets dispersed in PVA aqueous medium and a TEM photograph (c) of ultrathin cross section of the RuO_4-stained composite particles. All observations show that the obtained composite particles had a dent. In Fig. 1c, where RuO_4 stains PS but not PMMA [20], a PS phase was covered with a PMMA phase and the dent structure was observed only at the PS phase.

Figure 2 shows CLSM photographs of the P(S-PM)/PMMA/toluene (1/9/120, initial weight ratio) droplets stored in the uncovered vessel for 0 and 6 h. Homogeneous structure was observed in the droplets before evaporation of toluene. After 6 h, heterogeneous structure consisting of P(S-PM)-rich core (light region) and PMMA-rich shell (dark region) was observed in almost all the droplets. These results indicate that phase separation proceeded in the droplets and resulted in ex-centered P(S-PM)-core/PMMA-shell composite particles. The dried P(S-PM)/PMMA composite particles had a similar dent structure as the PS/PMMA composite particles shown in Fig. 1.

Figure 3 shows the SEM photographs of PS/PMMA composite particles having different PS/PMMA ratios prepared by releasing toluene from PS/PMMA/toluene droplets (1/9/120~9/1/120, w/w/w) dispersed in PVA aqueous media. For all polymer compositions, almost all particles had a dent and the dent structures were observed only at the PS phase in each particle (data were omitted). With an increase in the PS ratio, the size of the dent became bigger.

Figures 4 and 5, respectively, show the SEM photographs of PS/PMMA composite particles prepared by releasing solvent from the polymers/solvent (1/12, w/w) droplets, and the TEM photographs of the ultrathin cross sections of the RuO_4-stained composite particles. As solvent, *p*-xylene [solubility parameter (SP),

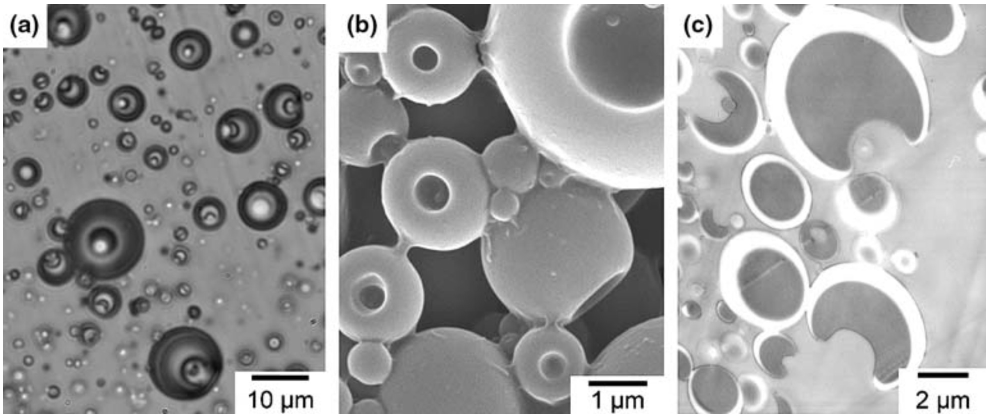

Fig. 1 An optical micrograph (**a**) and a SEM photograph (**b**) of PS/PMMA (1/1, w/w) composite particles, which were prepared by releasing toluene from the polymers/toluene (1/12, w/w) droplets dispersed in PVA aqueous medium in an uncovered cylindrical glass vessel, and a TEM photograph (**c**) of ultrathin cross section of the RuO_4-stained composite particles

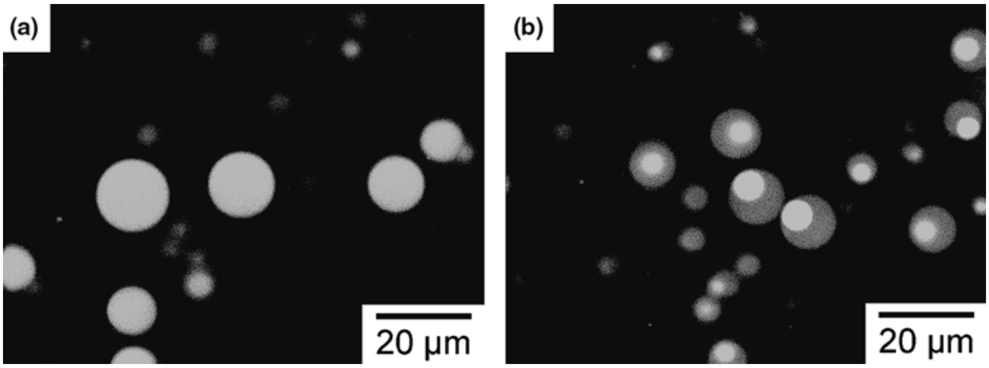

Fig. 2 Confocal laser scanning micrographs of poly(styrene-1-pyrenylmethyl methacrylate) [P(S-PM)] (S/PM = 200/1, w/w)/PMMA/toluene (1/9/120, initial weight ratio) droplets dispersed in PVA aqueous medium in an uncovered glass cylindrical vessel at 0 (**a**) and 6 h (**b**). P(S-PM)/PMMA/toluene (w/w/w): **a** 1/9/120, **b** 1/9/50

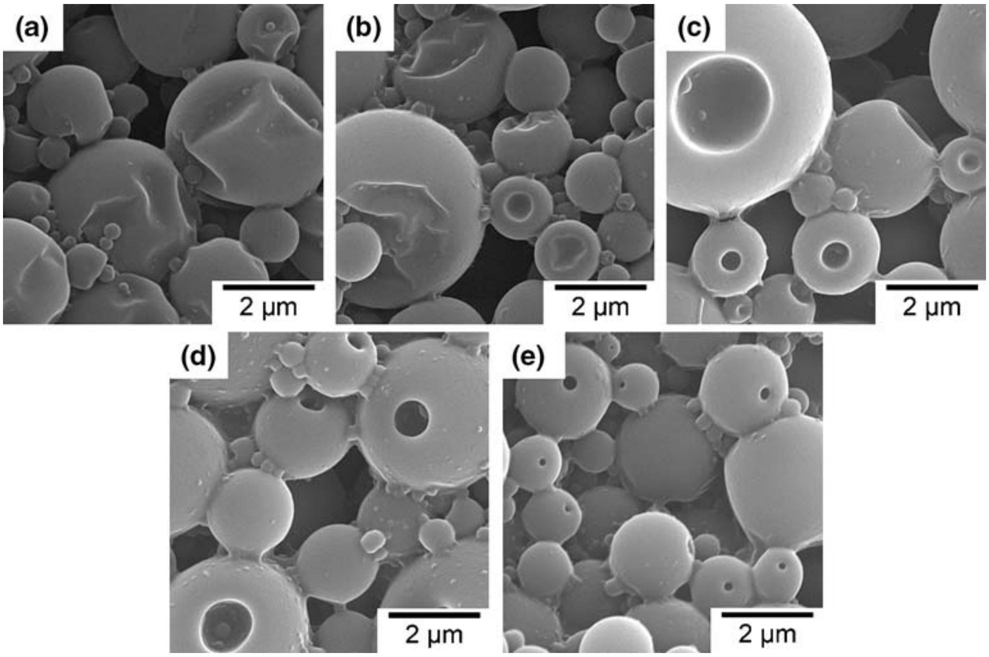

Fig. 3 Scanning electron microscope photographs of PS/PMMA composite particles which were prepared by releasing toluene from the polymers/toluene (1/12, w/w) droplets. PS/PMMA (w/w): **a** 9/1, **b** 7/3, **c** 5/5, **d** 3/7, **e** 1/9

18.0 $MPa^{1/2}$], ethylbenzene (18.0), toluene (18.2), benzene (18.8), and chloroform (19.0) were used. The SP values were quoted from a reference [21]. When the SP of the solvent was close to that of PS (SP, 17.5∼18.5 $MPa^{1/2}$), large dents were observed at the PS phase as shown in Fig. 5. On the other hand, in the case

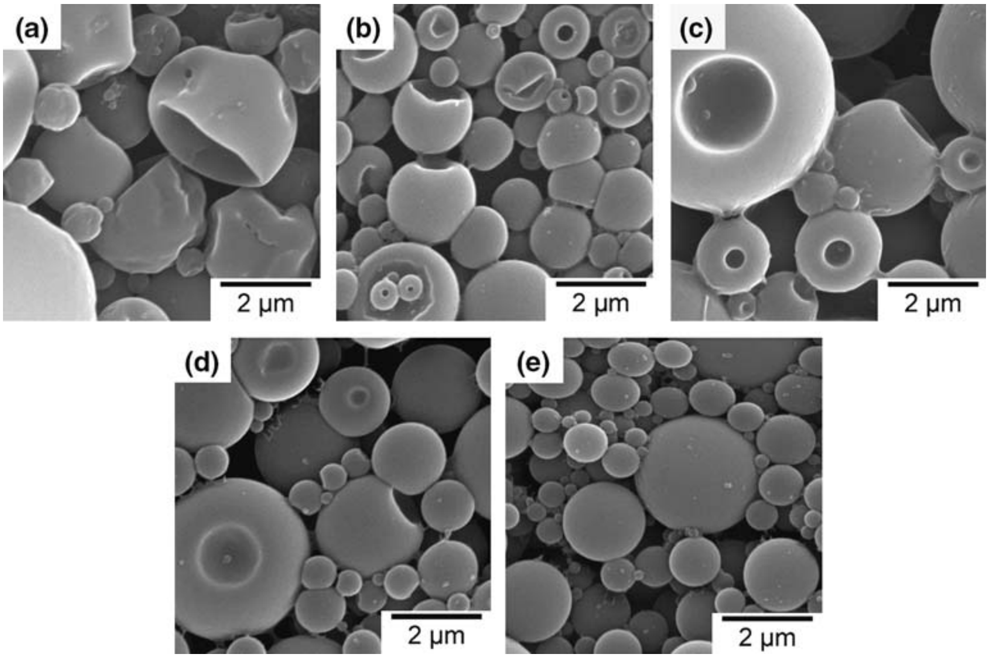

Fig. 4 Scanning electron microscope photographs of PS/PMMA (1/1, w/w) composite particles which were prepared by releasing the solvent from polymers/solvent (1/12, w/w) droplets. Solvents: **a** *p*-xylene, **b** ethylbenzene, **c** toluene, **d** benzene, **e** chloroform

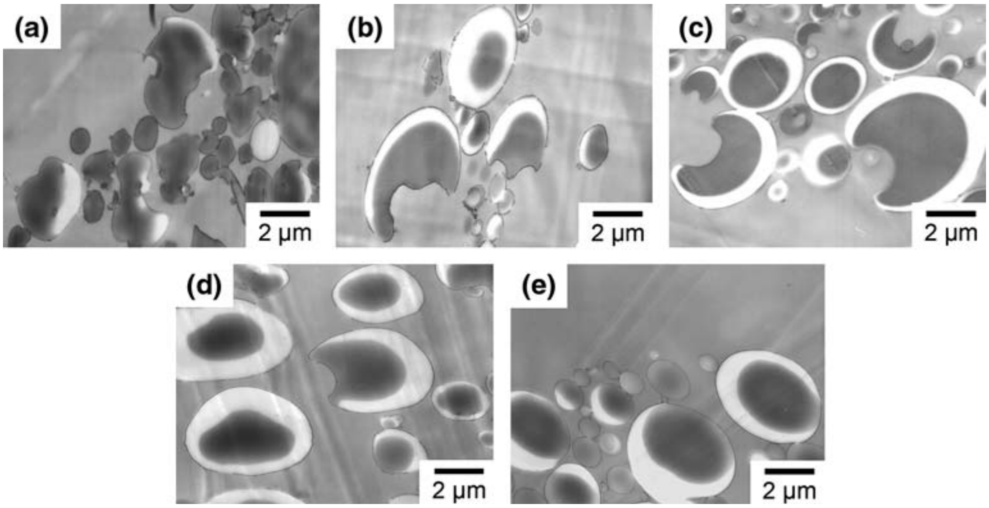

Fig. 5 Transmission electron microscope photographs of ultrathin cross sections of the RuO_4-stained PS/PMMA (1/1, w/w) composite particles, which were prepared by releasing the solvent from the polymers/solvent (1/12, w/w) droplets. Solvents: **a** *p*-xylene, **b** ethylbenzene, **c** toluene, **d** benzene, **e** chloroform

of chloroform, of which the SP was much closer to that of PMMA (SP, 18.5∼19.5 $MPa^{1/2}$), spherical ex-centered P(S-PM)-core/PMMA-composite particles were obtained. These results suggest that the affinity between the solvent and each polymer is greatly influenced on the morphology of the composite particles. The affinity between the solvent and each polymer is probably related to the partition of the solvent between two phases after the phase separation. In order to confirm this point, phase diagrams of the PS/PMMA/solvent were constructed.

Figure 6 shows the phase diagrams of PS/PMMA/ethylbenzene and PS/PMMA/chloroform systems. Arrows in the diagrams indicate the variation of each composition on the way of solvent evaporation in both systems. In the case of ethylbenzene as shown in Fig. 6a, when phase separation occurred in the droplet, the amount of ethylbenzene in the PS-rich phase was more than that in the PMMA-rich phase and this partition ratio of ethylbenzene would not change until the end of ethylbenzene evaporation. On the other hand, in the case of chloroform as shown in Fig. 6b, the amount of chloroform in the PS-rich phase was less than that of the PMMA-rich phase until the end of chloroform evaporation. These results suggest that in the case of solvent partitioned more in the PS-rich core than in the PMMA-rich shell, the obtained particles would have dent structure. That is, it seems that the PMMA-rich shell is

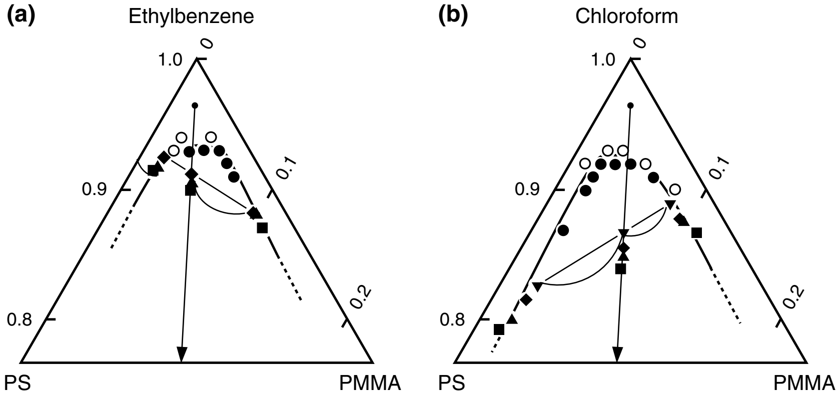

Fig. 6 Phase diagrams of PS/PMMA/ethylbenzene (**a**) and PS/PMMA/chloroform (**b**) for the volume ratios at 20 °C. *Closed* and *open symbols* indicate, respectively, heterogeneous (*filled circle*) and homogeneous (*open circle*) solutions. PS/PMMA/solvent (w/w/w): 1/1/14 (*filled square*), 1/1/15 (*filled triangle*), 1/1/16 (*filled diamond*), 1/1/17 (*filled inverted triangle*)

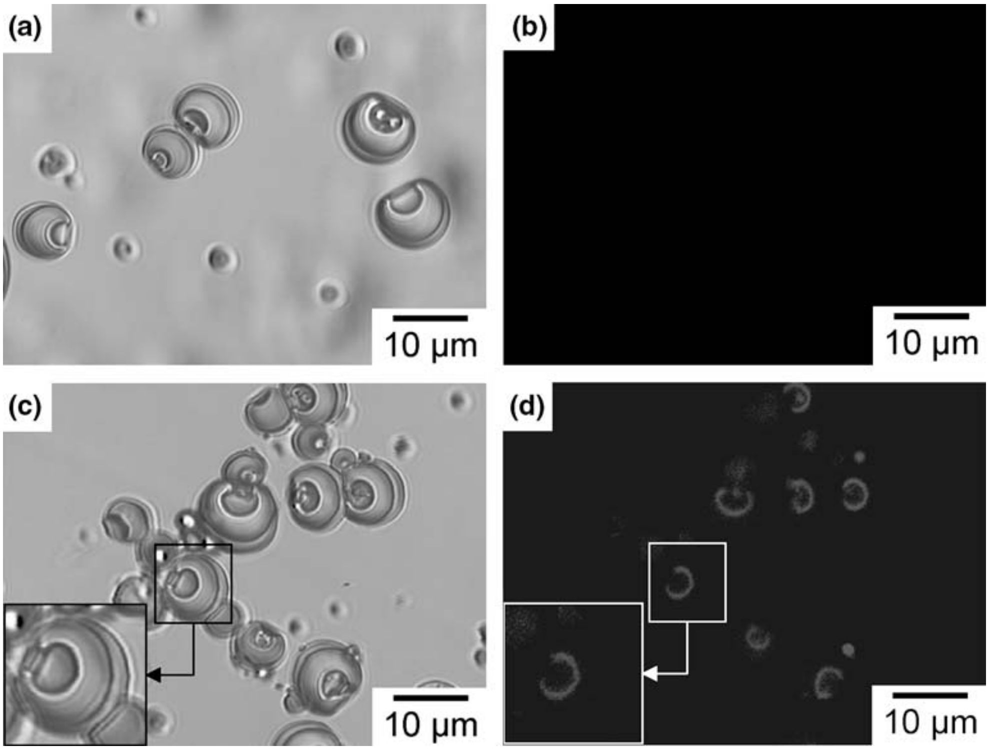

Fig. 7 Optical (**a**, **c**) and confocal laser scanning (**b**, **d**) micrographs of CH_3NH_2-treated PS/PMMA (5/5, w/w) (**a**, **b**) and CH_3NH_2-modified P(S-CMS)/PMMA (5/5, w/w) (**c**, **d**) composite particles after reaction with the fluorescence dye (DIDS) (polymers/DIDS = 5/2, w/w) for 100 h

hardened prior to the PS-rich core in the process of solvent evaporation and then the solvent evaporation from the PS-rich core results in the dent structure. On the other hand, in the case of the solvent that partitioned more in the PMMA-rich shell than in the PS-rich core, spherical particles would be obtained.

The CLSM results shown in Fig. 2 indicate that the PS/PMMA/toluene droplets had an ex-centered PS-core/PMMA-shell morphology, in which a part of the PS core seems to be in contact with the aqueous medium. In order to clarify this point, P(S-CMS)/PMMA (1/1, w/w) composite particles, which were prepared from toluene droplets in a similar way and had the dent structure, were dispersed in CH_3NH_2 aqueous solution, and then in DIDS (fluorescent dye) aqueous solution in sequence and a CLSM observation was conducted. The amination of chloromethyl functional group with CH_3NH_2 seems to be restricted only at the particle surface because CH_3NH_2 cannot diffuse into the particle. Therefore, if a part of the P(S-CMS) core in the P(S-CMS)/PMMA composite particles makes contact with the aqueous medium, the chloromethyl functional group thereon could react with CH_3NH_2.

Figure 7 shows the optical micrographs and the CLSM photographs of CH_3NH_2-treated PS/PMMA and CH_3NH_2-modified P(S-CMS)/PMMA composite particles after reaction with the fluorescence dye (DIDS) for 100 h. As shown in Fig. 7d, the CH_3NH_2-

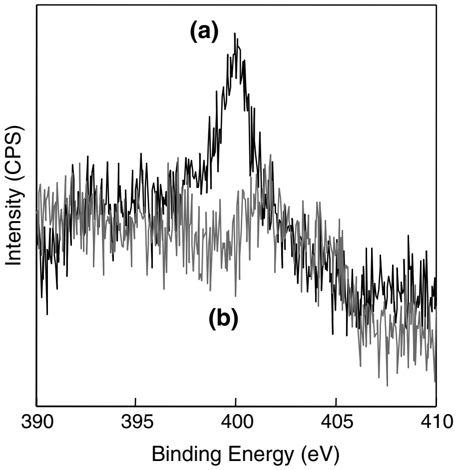

Fig. 8 N_{1s} X-ray photoelectron spectra of PCMS particles before (**a**) and after (**b**) the argon ion sputtering for 120 s, after aminated with CH_3NH_2 in aqueous medium. Acceleration voltage: 2.0 kV, ion beam current: 20 mA

modified P(S-CMS)/PMMA composite particles after the reaction with the fluorescence dye fluoresced at the surface of dent. On the other hand, as shown in Fig. 7b, the CH_3NH_2-treated PS/PMMA composite particles hardly fluoresce though the treatment was conducted in the same manner as that in Fig. 7d. This indicates that the fluorescence at the surface of the dent of the P(S-CMS)/PMMA composite particles shown in Fig. 7d was due to nonadsorption of the fluorescence dye, but the surface reaction of the amino group with the fluorescence dye. These results suggest that the PS/PMMA composite particles having the dent had an incomplete core–shell structure, in which the PS core was not perfectly covered by the PMMA shell. However, this deduction has still some uncertainty. If both, the amination with CH_3NH_2 and the subsequent reaction with fluorescence dye occurred not only at the particle surface but also in the inside, the P(S-CMS)/PMMA composite particles would fluoresce even if they had a complete core–shell structure. In order to remove this uncertainty, an additional experiment was carried out as follows.

Figure 8 shows the N_{1s} X-ray photoelectron spectra of the PCMS particles before and after the argon ion sputtering, after being aminated with CH_3NH_2 in the aqueous medium. The detection of N_{1s} signal before the sputtering shown in Fig. 8a indicates that the amination of the chloromethyl group at the PCMS particle surface with CH_3NH_2 was surely attained. On the other hand, after the argon ion sputtering shown in Fig. 8b, the N_{1s} signal disappeared. These results indicate that the amination did not proceed inside the particles, because the argon ion sputtering could not etch deeper under the conditions described in the experimental section. Therefore, it was concluded that a part of the PS core in the PS/PMMA composite particles having the dent shown in Fig. 1 made contact with the aqueous medium.

From these results, the formation mechanism of the PS/PMMA composite particles having the dent is explained as shown in Fig. 9. First, phase separation occurs in the PS/PMMA/toluene droplets on the way of toluene evaporation, resulting in the ex-centered PS-core/PMMA-shell structure. The PMMA shell is hardened prior to the PS core, because the PMMA shell contains less toluene than the PS core. After the PMMA shell is hardened, shrinkage of the PS core with the release of the residual toluene therein makes a cave-in at the surface of the PS core that contacts with the aqueous medium. Therefore, the more the toluene partition in the PS core increases, the bigger the size of the dent becomes. The reason for a part of PS core making contact with the aqueous medium will be discussed in the near future.

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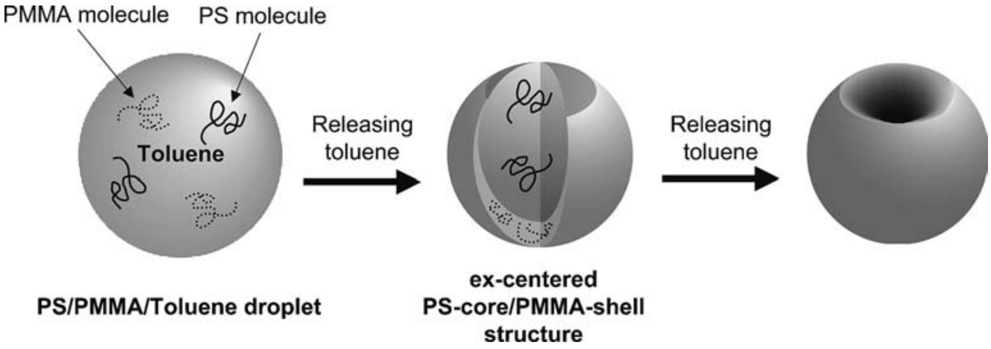
Fig. 9 Schematic model of the formation mechanism of PS/PMMA composite particle having a dent



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