Formation of Dented Poly(methyl methacrylate)/Poly(styrene-*co*-divinylbenzene) Composite Particles in Seeded Soap-free Emulsion Copolymerization

Shan Shi,[1,2] Hiroaki Hayami,[1] Shin-ichi Kuroda,*[1] and Hitoshi Kubota[1]
[1]*Department of Chemistry, Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515*
[2]*Department of Materials Science and Engineering, Shenyang Institute of Chemical Technology, Shenyang 110142, P. R. China*

(Received December 28, 2005; CL-051580; E-mail: skuroda@chem.gunma-u.ac.jp)

Nonspherical composite particles having multiple dents on particle surface were synthesized for the first time by seeded soap-free emulsion copolymerization of styrene and divinylbenzene (crosslinker) on spherical, linear poly(methyl methacrylate) seed particles. The number and depth of the dents were controllable by varying polymerization formulation.

There has been increased interest in the fabrication of nonspherical particles of submicron and micron size in recent years.[1–3] Seeded emulsion (co)polymerization is a frequently employed strategy to prepare the submicron-sized nonspherical particles.[2,3] In many cases, the preparation of nonspherical particles by this technique is based on the use of a crosslinked seed polymer which causes the phase separation of the second-stage polymer from the seed polymer during seeded emulsion polymerization process.[3]

In this paper, a novel preparation technique, i.e., the formation of nonspherical particles by crosslinking the second-stage polymer in seeded soap-free emulsion copolymerization is briefly reported. The styrene (St) and divinylbenzene (DVB, used as a crosslinker) were copolymerized onto the spherical, linear poly(methyl methacrylate) (PMMA) seed particles and the resulting PMMA/poly(St-*co*-DVB) (PMMA/P(St-*co*-DVB)) composite latex particles were characterized. Several research groups have recently described the copolymerization of a vinyl monomer with a divinyl monomer in the presence of seed particles, but no mention was made of the formation of nonspherical particles.[4]

All polymerizations were carried out in a 300-mL four-neck, round-bottom separated flask equipped with a mechanical marine-type agitator, a nitrogen inlet and a sampling syringe. PMMA seed latex particles, which have a number-average diameter of 413 nm with a good monodisperity (Cv = 3.6%), were prepared via a standard soap-free emulsion polymerization at 70 °C for 5 h. The seed latex was dialyzed against deionized water for 3 days before use. A typical experimental procedure for seeded soap-free emulsion copolymerization was as follows. Prescribed amount of PMMA seed polymer, deionized water and potassium persulfate (KPS, used as a radical initiator) were charged into the flask and bubbled with nitrogen gas for 30 min under stirring. Then, the oxygen-free St monomer and DVB (55% meta and para isomers) were added, followed by the initiation of the seeded copolymerization by immersing the flask into the water bath thermostated at 60 °C. The seeded soap-free emulsion copolymerization was carried out for 6 h with continuous stirring of 250 rpm. The kinetic study revealed that the seeded copolymerization almost finished within 1 h and the final monomer conversion attained was about 80% or higher.

All the seeded soap-free emulsion copolymerizations were found to progress without appreciable agglomeration. The prepared PMMA/P(St-*co*-DVB) composite particles were freeze-dried and subjected to Fourier transform infrared spectroscopy (FT-IR, JASCO FT/IR-8000) analysis. A distinct peak near 700 $\mathrm{cm^{-1}}$ (characteristic absorption of aromatic C–H bending) was detected in the FT-IR spectra, suggesting that the second-stage P(St-*co*-DVB) polymer was successfully introduced into PMMA seed particles (no new P(St-*co*-DVB) particles were formed in the seeded polymerization as shown below). The composite particles were observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) after sputter-coating with gold (150 Å). Figure 1 shows the FE-SEM micrographs of PMMA/P(St-*co*-DVB) composite particles prepared by using different concentrations of DVB crosslinker. In contrast to the smooth-surfaced spherical particles prepared without any DVB in seeded polymerization (Figure 1a), the nonspherical particles with multiple dents on their surface were obtained when 0.6, 2.5, and 4.9% DVB were copolymerized to the second-stage polymer polystyrene (PSt) (Figures 1b–1d). The number and depth of the dents increased as the DVB concentration increased, though the exact quantification is difficult. It is also obvious from FE-SEM that the seeded copolymerization proceeded in the absence of secondary nucleation of new particles because no by-produced P(St-*co*-DVB) particles were observed.

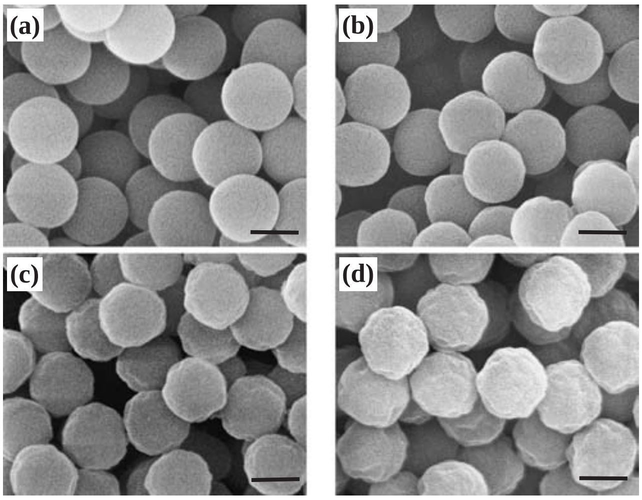

Figure 1. FE-SEM micrographs of PMMA/P(St-*co*-DVB) composite particles prepared by seeded soap-free emulsion copolymerization using DVB concentrations (wt %, based on St) of: (a) 0%, (b) 0.6%, (c) 2.5%, and (d) 4.9%. PMMA seed polymer: 0.6 g, St: 1.46 g, deionized water: 130 mL, KPS: 20 mg, temperature: 60 °C. Scale bar: 400 nm.

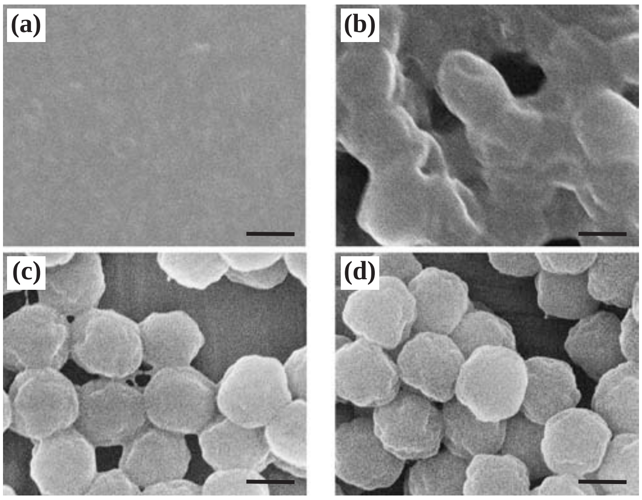

Figure 2. FE-SEM micrographs of THF-cast films of PMMA/P(St-*co*-DVB) composite particles prepared by seeded soap-free emulsion copolymerization using DVB concentrations (wt %, based on St) of: (a) 0%, (b) 0.6%, (c) 2.5%, and (d) 4.9%. PMMA seed polymer: 0.6 g, St: 1.46 g, deionized water: 130 mL, KPS: 20 mg, temperature: 60 °C. Scale bar: 400 nm.

To confirm whether a 3-D network had been effectively formed in PMMA/P(St-*co*-DVB) composite particles, the solubility of the composite particles in tetrahydrofuran (THF) was studied. 0.01 g of freeze-dried particles and 1.99 g of THF were weighed into a capped 50-mL vial to give 0.5% dispersion, which were then shaken horizontally (100 cycles/min) at ambient temperature for 10 days. The particles prepared without addition of DVB dissolved completely and gave a clear dispersion; however, those prepared with addition of 0.6, 2.5, and 4.9% DVB did not dissolved completely and gave turbid dispersions. These clear and turbid dispersions were cast directly on FE-SEM stud and examined by FE-SEM. As shown in Figure 2, the former yielded a smooth film (Figure 2a), but the latter yielded discontinuous films which consisted of particles embedded in amorphous matrix (Figure 2b) or connected with small tendrils (Figures 2c and 2d). In particular, the composite particles with 0.6% DVB addition considerably distorted, whereas those with 4.9% DVB addition almost retained their as-polymerized surface morphology. These results indicated that a crosslinked network was successfully developed by copolymerization of DVB crosslinker with St during seeded soap-free emulsion copolymerization, and the more DVB crosslinker added, the more were the gel fractions contained.

Figure 3 shows the effect on particle morphology of changing the amount of St added in seeded copolymerization while maintaining the other polymerization conditions. Reducing the St amount from 1.46 g (seed/monomer = 1:2.4) to 0.6 g (seed/monomer = 1:1) produced normal spherical composite particles (Figure 3a). On the contrary, increasing the St amount to 2.5 g (seed/monomer = 1:4) resulted in the composite particles having severely deformed surface morphology. Accordingly, it seems that a sufficient amount of the second-stage monomers is necessary to prepare the dented PMMA/P(St-*co*-DVB) composite particles by the present technique.

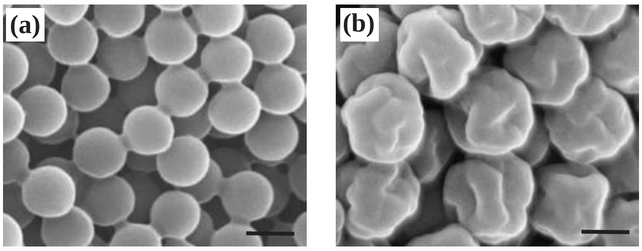

Figure 3. FE-SEM micrographs of PMMA/P(St-*co*-DVB) composite particles prepared by seeded soap-free emulsion copolymerization with addition amounts of St of: (a) 0.6 g, and (b) 2.5 g. PMMA seed polymer: 0.6 g, DVB: 4.9% (wt %, based on St), deionized water: 130 mL, KPS: 20 mg, temperature: 60 °C. Scale bar: 400 nm.

Based on the foregoing description, it is evident that the formation of the dented PMMA/P(St-*co*-DVB) composite particles is a direct result of the introduction of crosslinked network into the second-stage PSt polymer. Once the crosslinked PSt network was developed around PMMA seed particle during seeded copolymerization,[5] it tended to be swollen by absorbing the unreacted monomers, and subsequently contract as the monomers polymerized to relax the network polymer chains. However, the uneven crosslinking structure of PSt network led to uneven contraction of growing particles. As a result, the composite particles with multiple dents were formed at the end of the polymerization. Our ongoing study has demonstrated that this swelling and contracting process depended strongly on the polymerization temperature, the addition mode of the second-stage monomers, and the property of PMMA seed particles. The effect of these polymerization parameters on the surface morphology as well as the kinetic study will be detailed in a forthcoming article.

References and Notes

1 a) S. Shi, S. Kuroda, K. Hosoi, H. Kubota, *Polymer* **2005**, *46*, 3567. b) R. G. Alargova, K. H. Bhatt, V. N. Paunov, O. D. Vele, *Adv. Mater.* **2004**, *16*, 1653. c) Z. Nie, S. Xu, M. Seo, P. C. Lewis, E. Kumacheva, *J. Am. Chem. Soc.* **2005**, *127*, 8058. d) Y. Lu, Y. Yin, Y. Xia, *Adv. Mater.* **2001**, *13*, 415. e) Z. Q. Sun, X. Chen, J. H. Zhang, Z. M. Chen, K. Zhang, X. Yan, Y. F. Wang, W. Z. Yu, B. Yang, *Langmuir* **2005**, *21*, 8987. f) F. M. Bauers, R. Thomann, S. Mecking, *J. Am. Chem. Soc.* **2003**, *125*, 8838. g) L. Zhou, S. Shi, S. Kuroda, H. Kubota, *Chem. Lett.* **2006**, *35*, 248.

2 a) S. Reculusa, C. Mingotaud, E. Bourgeat-Lami, E. Duguet, S. Ravaine, *Nano Lett.* **2004**, *4*, 1677. b) S. Reculusa, C. Poncet-Legrand, S. Ravaine, C. Mingotaud, E. Duguet, E. Bourgeat-Lami, *Chem. Mater.* **2002**, *14*, 2354.

3 a) S. Shi, S. Kuroda, H. Kubota, *Colloid Polym. Sci.* **2003**, *281*, 331. b) Y. Z. Du, T. Tomohiro, M. Kodaka, *Macromolecules* **2004**, *37*, 803.

4 a) L. Bouvier-Fontes, R. Pirri, J. M. Asua, J. R. Leiza, *Macromolecules* **2005**, *38*, 1164. b) S. Fujii, D. P. Randall, S. P. Armes, *Langmuir* **2004**, *20*, 11329. c) A. M. Santos, A. Elaissari, J. M. G. Martinho, C. Pichot, *Polymer* **2005**, *46*, 1181. d) W. F. Liu, Z. X. Guo, J. Yu, *J. Appl. Polym. Sci.* **2005**, *97*, 1538. e) L. Bouvier-Fontes, R. Pirri, S. Magnet, J. M. Asua, J. R. Leiza, *Macromolecules* **2005**, *38*, 2722.

5 The internal morphology of PMMA/P(St-*co*-DVB) composite particles was examined by transmission electron microscopy (TEM, JEOL JEM-1200EXII) on the ultrathin cross-sections (ca. 60 nm in thickness; P(St-*co*-DVB) phase was stained dark with RuO_4 vapor). It was observed that all the composite particles had a core/shell structure. P(St-*co*-DVB)-rich phase formed the shell encasing the PMMA-rich core.

Published on the web (Advance View) February 18, 2006; DOI 10.1246/cl.2006.320