

Formation of Pickering Emulsions Stabilized via Interaction between Nanoparticles Dispersed in Aqueous Phase and Polymer End Groups Dissolved in Oil Phase

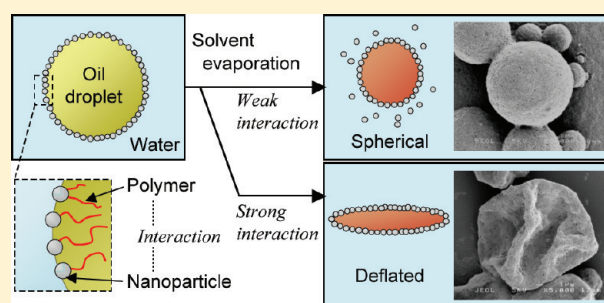
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S Supporting Information

ABSTRACT: The influence of end groups of a polymer dissolved in an oil phase on the formation of a Pickering-type hydroxyapatite (HAp) nanoparticle-stabilized emulsion and on the morphology of HAp nanoparticle-coated microspheres prepared by evaporating solvent from the emulsion was investigated. Polystyrene (PS) molecules with varying end groups and molecular weights were used as model polymers. Although HAp nanoparticles alone could not function as a particulate emulsifier for stabilizing dichloromethane (oil) droplets, oil droplets could be stabilized with the aid of carboxyl end groups of the polymers dissolved in the oil phase. Lower-molecular-weight PS molecules containing carboxyl end groups formed small droplets and deflated microspheres, due to the higher concentration of carboxyl groups on the droplet/microsphere surface and hence stronger adsorption of the nanoparticles at the water/oil interface. In addition, Pickering-type suspension polymerization of styrene droplets stabilized by PS molecules containing carboxyl end groups successfully led to the formation of spherical HAp-coated microspheres.



1. INTRODUCTION

Pickering emulsions are solid particle-stabilized emulsions, in which solid particles are adsorbed onto oil/water interfaces.¹ Inorganic particles (such as silica,² clay,³ and carbon black⁴), organic particles (such as latex⁵ and microgels⁶), and Janus particles^{3b,7} have been used as particulate emulsifiers. The stability and type of emulsion [oil-in-water (O/W) or water-in-oil (W/O)] depend on particle wettability (contact angle, θ) at the oil/water interface;^{8,9} for example, highly hydrophilic ($\theta \ll 90^\circ$) or highly hydrophobic silica ($\theta \gg 90^\circ$) particles cannot stabilize emulsions, relatively hydrophilic silica particles ($\theta < 90^\circ$) preferentially stabilize O/W emulsions, and relatively hydrophobic silica particles ($\theta > 90^\circ$) preferentially stabilize W/O emulsions. To obtain stable Pickering-type emulsions, most studies have used surface-modified particulate emulsifiers,^{8–10} or have modified particulate emulsifiers in situ by adding surface-active molecules in continuous phases.^{11–13}

These solid-stabilized emulsion droplets can be used as a platform toward functional materials such as composite microspheres and Janus particles. For examples, Pickering-type suspension polymerization,¹⁴ inversed suspension polymerization,¹⁵ and mini-emulsion polymerization¹⁶ were proven to be a powerful method to prepare composite microspheres. Granick and co-workers prepared silica-coated paraffin microspheres by cooling silica-stabilized paraffin droplets (molten liquid), and the composite microspheres were used to

synthesize Janus silica particles by modifying the silica particulate emulsifiers on the microspheres.^{2a,b} Zhang et al. prepared silica-coated polystyrenes (PS) microspheres by evaporating toluene from silica-stabilized toluene droplets dissolving PS, and the microspheres were also used for synthesizing Janus silica particles.^{2d}

We have explored the possibility of hydroxyapatite (HAp; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) nanoparticles as a particulate emulsifier.¹⁷ HAp is the main mineral of bones and teeth, and artificially synthesized HAp has been extensively used in a variety of applications such as biomaterials, ion exchangers, adsorbents, and catalysts.¹⁸ It was found that HAp-nanoparticle-stabilized O/W emulsions were readily obtained using oils containing an ester group (e.g., methyl myristate); however, no stable emulsion was obtained using oils without an ester group (e.g., dichloromethane).¹⁷ Furthermore, dichloromethane droplets could be successfully stabilized with HAp nanoparticles by dissolving polymer molecules containing ester groups (such as biodegradable poly-L-lactide) in dichloromethane^{17,19} via interactions between nanoparticles and polymer molecules at oil/water interfaces. Spherical biodegradable polymer microspheres coated with HAp could be prepared by evaporation of

Received: April 19, 2012

Revised: May 22, 2012

Published: May 22, 2012



dichloromethane from the HAp-stabilized dichloromethane droplets dissolving polyesters.^{19,20} The HAp-coated biodegradable microspheres showed improved cell adhesion properties and were suitable as injectable cell scaffolds for tissue engineering applications.²¹

In a previous article,²⁰ Fourier-transform infrared (FT-IR) studies showed the interactions not only between HAp surfaces and main chains (ester groups) of the polyesters but also between HAp surfaces and end groups (carboxyl groups) of the polyesters. Carboxyl groups interact electrostatically with the calcium ion on HAp.²² Therefore, we hypothesized that HAp nanoparticle-stabilized emulsion droplets can be obtained by controlling the polymer end groups regardless of the type of polymer dissolved in the oil phase.

In this study, PS with varying end groups and molecular weights were used as model polymers to investigate the influence of polymer end groups on formation of HAp-nanoparticle-stabilized droplets/microspheres, and to extend the range of polymer types beyond polyesters used in previous studies.^{19,20} PS was selected because it is one of the most widely used plastics and does not contain ester groups in its main chain, unlike polyesters. The present study also determined the size of the oil droplets and the morphology (shape and the amount of HAp coating) of the microspheres by optical microscopy, scanning electron microscopy (SEM), laser diffraction particle size analysis, and thermogravimetric analysis (TG). Moreover, the suspension polymerization of styrene monomer droplets stabilized by HAp nanoparticles with the aid of PS molecules containing carboxyl groups dissolved in monomer droplets was demonstrated without the use of water-soluble surfactants or polymeric stabilizers.

2. EXPERIMENTAL SECTION

Materials. Reagent grade $(\text{NH}_4)_2\text{HPO}_4$ (Kishida Chemicals Co., Ltd., Osaka, Japan), 25% aq NH_3 (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and dichloromethane (Sigma Aldrich Co., St. Louis, MO) were used as received. Styrene monomer (Sigma Aldrich Co.) was used after passing through an inhibitor removal column (Sigma Aldrich Co.). 4,4'-Azobis(4-cyanovaleric acid) (ACVA; Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and 2,2'-azobisisobutyronitrile (AIBN; Nacalai Tesque Inc., Kyoto, Japan) initiators were used after recrystallization from ethanol. Water was purified with a Milli-Q system (Millipore Corp., Billerica, MA). Other chemicals were reagent grade and used as received from Nacalai Tesque Inc., Kyoto, Japan.

HAp Nanoparticles. Spherical HAp nanoparticles were prepared via a wet chemical method using a previously described process.¹⁷ Briefly, aq $\text{Ca}(\text{NO}_3)_2$ (42 mmol/L, 800 mL), with pH adjusted to 12.0 by addition of 25% ammonia solution, was poured into a reactor equipped with a N_2 inlet. After the reactor temperature had been equilibrated at 25 °C, aq $(\text{NH}_4)_2\text{HPO}_4$ (100 mmol/L, 200 mL) was added to the reactor within 10 s, and the mixture was stirred for another 24 h at 25 °C. The resulting HAp particles were centrifuged and washed repeatedly using Milli-Q water until the pH value of the supernatant decreased to approximately 7.

PS Molecules. Three types of PS molecules having COOH end groups (PS-COOH) and different molecular weights were prepared by solution polymerization of styrene (12.7 mol/L) and varying concentrations of ACVA initiator (5, 25, 125 mmol/L) in tetrahydrofuran at 69 °C for 20 h (see Supporting Information Table S1). After polymerization, the polymers were purified by several dissolution/precipitation cycles using tetrahydrofuran as a solvent and methanol as a nonsolvent, followed by drying under a vacuum at room temperature. As a control, PS molecules with no carboxyl groups (PS- CH_3) were prepared with AIBN initiator (25 mmol/L) at 65 °C and purified in the same manner.

The molecular weight of PS molecules was measured using gel permeation chromatography (GPC; HLC-8220GPC; TOSOH Corp., Tokyo, Japan) with chloroform as the solvent and was calibrated with polystyrene standards (UBE Scientific Analysis Laboratory, Inc., Tokyo, Japan). Weight-averaged molecular weight (M_w) and number-averaged molecular weight (M_n) of the three types of PS-COOH determined by GPC measurements were: $M_n = 16\,400$ ($M_w/M_n = 3.9$), $M_n = 2200$ ($M_w/M_n = 11.4$), and $M_n = 800$ ($M_w/M_n = 8.5$), referred to as PS_H-COOH, PS_M-COOH, and PS_L-COOH, respectively (see Supporting Information Table S1). M_w and M_n of PS- CH_3 prepared as a control polymer with AIBN initiator were: $M_n = 2800$ ($M_w/M_n = 6.2$).

The number of styrene units per two carboxyl groups of PS-COOH was estimated from FT-IR peak intensity ratio between overtones of monosubstituted benzenes in styrene units (1872 cm^{-1}) and C=O stretching vibrations (1708 cm^{-1}) using Spectrum One (Perkin-Elmer Inc., MA) with a diffuse reflectance unit at a resolution of 4 cm^{-1} and 16 scans at room temperature. A calibration curve was first established with the mixtures of ACVA and PS- CH_3 , by plotting the peak intensity ratio against the molar ratio of carboxyl groups of ACVA and styrene monomer units of PS- CH_3 .

The interaction between the HAp nanoparticles and PS molecules was investigated by examining FT-IR spectra of HAp/PS mixtures using a diffuse reflectance unit at a resolution of 4 cm^{-1} over 16 scans at room temperature. The mixture was prepared by dispersing the HAp nanoparticles (0.1 g) in a dichloromethane solution containing PS (0.3 g), followed by drying in air at room temperature and then under reduced pressure.

Emulsions and Microspheres. Stock aqueous dispersions of HAp nanoparticles with a solid content of 0.04 wt % were prepared; the pH of the dispersion was 6.5 (measured with a pH meter). Aliquots of these dispersions (25 g) were mixed with the dichloromethane solution of PS (total 2.5 g; 0.01–10 wt % solid content) in a glass tube (outer diameter, 40 mm; glass thickness, 1.8 mm; height, 75 mm; Nichiden-Rika Glass Co., Ltd., Kobe, Japan) using a Vortex-Genie 2 mixer (Scientific Industries, Inc., NY) at maximum rotation speed (approximately 3200 rpm) for 1 min at room temperature (ca. 20 °C). The HAp/PS composite microspheres were prepared by evaporating dichloromethane from the emulsions at room temperature for 24 h under magnetic stirring.

A drop of the diluted emulsion was placed on a microscope slide and observed under an optical microscope (Eclipse TE2000-U; Nikon Corp., Tokyo, Japan) fitted with a digital camera (Nikon DXM1200F). The mean droplet (or microsphere) size in the aqueous medium was determined from circle equivalent diameters of the droplets ($n = 300$) using ImageJ software (National Institutes of Health, Bethesda, MD). Each size is expressed as mean \pm standard deviation (SD).

The surfaces of the microspheres were observed with a JSM-6301F SEM (Jeol Ltd., Tokyo, Japan) operating at 5 kV, after the samples were dried on an aluminum stub and sputter coated with gold to minimize sample-charging problems.

The TG analysis of HAp nanoparticle-coated PS microspheres was conducted with a SII Nanotechnology TG/DTA6300 analyzer (Seiko Instruments Inc., Chiba, Japan) after the microspheres were washed; the white dispersions obtained after dichloromethane evaporation were purified by at least four sedimentation–redispersion cycles, with each successive supernatant being decanted and replaced with water until excess free HAp nanoparticles was no longer observed by SEM. The dried microspheres after purification were heated from 35 to 600 °C at a scanning rate of 10 °C/min under nitrogen.

Suspension Polymerization. Suspension polymerization of styrene monomer droplets stabilized with a combination of HAp nanoparticles and PS molecules was conducted as follows. A total of 30 g of aqueous dispersion of HAp nanoparticles (0.33 wt %) was mixed with 3.0 g of styrene monomer containing PS_L-COOH (0.03 g) and AIBN (0.03 g) using a Vortex-Genie 2 mixer at a maximum rotation speed (approximately 3200 rpm) for 1 min at room temperature. The mixture was poured into a glass tube, which was then purged with N_2 . The glass tube was sealed, immersed into a water bath at 65 °C to initiate polymerization, and shaken at 60 cycles/min (3 cm strokes).

After 12 h polymerization, the glass tube was removed from the water bath and cooled in ice water. Conversion of styrene monomer was estimated from the solid content measured by drying the suspension after adding 0.1 wt % aq hydroquinone to prevent further polymerization.

3. RESULTS AND DISCUSSION

HAp Nanoparticles and PS Molecules. The spherical HAp nanoparticles prepared by the wet chemical method had a number-average diameter of 39 ± 7 nm (see Supporting Information Figure S1). Laser light scattering studies of highly dilute aqueous dispersions of the HAp nanoparticles at pH 6.5 indicated that their intensity-average diameter was greater than 100 nm rather than 39 nm, and the diameter distribution was broad even after intensive sonication for 1 h. This colloidal instability may be due to low ζ -potential at pH 6.5,^{17,23} which can lead to weak flocculation. The HAp nanoparticles were used as a particulate emulsifier in their weakly flocculated states; good emulsion stability can be achieved when the particles are weakly flocculated.²⁴

Figure 1 shows FT-IR spectra of PS-CH₃, PS_H-COOH, PS_M-COOH, and PS_L-COOH. The FT-IR spectrum of pure PS-CH₃

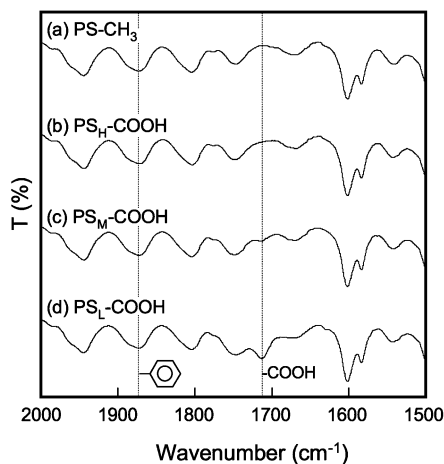


Figure 1. FT-IR spectra of (a) PS-CH₃, (b) PS_H-COOH, (c) PS_M-COOH, and (d) PS_L-COOH prepared by solution polymerization of styrene with different initiators: (a) AIBN and (b–d) ACVA.

(Figure 1a) showed typical absorption bands of PS (aromatic overtone and combination bands in 2000–1670 cm^{−1} region; C=C stretching vibrations at 1606 cm^{−1}). The FT-IR spectrum of pure PS_L-COOH (Figure 1d) showed an additional absorption at 1710 cm^{−1} assigned to carboxyl groups, and peak height increased with a decrease in molecular weight (Figure 1b–d; see also Supporting Information Figure S2). The numbers of styrene units per two carboxyl groups, estimated from FT-IR studies, were 160 for PS_H-COOH ($M_n = 16400$), 36 for PS_M-COOH ($M_n = 2200$), and 16 for PS_L-COOH ($M_n = 800$). These numbers are roughly similar to those calculated from M_n values (obtained from GPC measurements) under the assumption that each molecule contains two carboxyl end groups (PS radicals terminate predominantly by combination rather than by disproportionation²⁵).

The interaction between HAp nanoparticles and PS molecules was estimated by conducting measurements of FT-IR spectra of their mixtures (Figure 2). The FT-IR spectrum of the HAp/PS-CH₃ mixture was the same as that of pure PS-

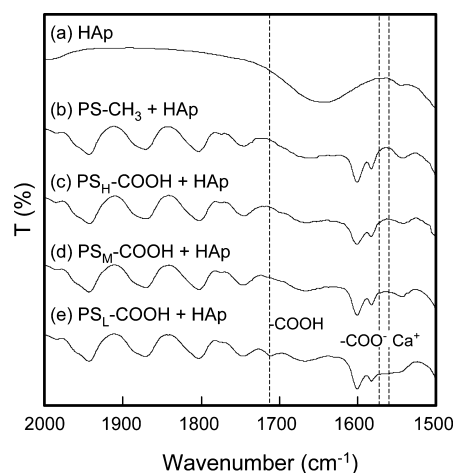


Figure 2. FT-IR spectra of (a) pure HAp nanoparticles, and mixtures of HAp and PS molecules: (b) PS-CH₃, (c) PS_H-COOH, (d) PS_M-COOH, and (e) PS_L-COOH.

CH₃; no new peak or peak shift was observed (Figure 2b; see also Supporting Information Figure S3). In contrast, the intensity of the peak at 1710 cm^{−1} assigned to the carboxyl groups in the HAp/PS_L-COOH mixture (Figure 2e) decreased, and a new broad adsorption peak appeared at ca. 1560–1570 cm^{−1}, assigned to carboxylate groups interacting with Ca²⁺ ions on the surface of HAp.²⁶ These results indicate that the carboxyl end groups of PS molecules have an affinity for the HAp surface.

Emulsion Formation. Figure 3 summarizes the digital photographs of the mixtures in dichloromethane and water. Only the mixture of the dichloromethane solution of PS_M-COOH and the aqueous dispersion of HAp nanoparticles formed a stable milky emulsion (Figure 3f). The other control systems failed to produce stable emulsions (homogenized oil droplets coalesced into large domains within a short time period): homogenization of pure dichloromethane and pure water (Figure 3a; absence of HAp and PS); homogenization of pure dichloromethane and the aqueous dispersion of the HAp nanoparticles (Figure 3b; absence of PS); and homogenization of the dichloromethane solution of PS and pure water (Figure 3c and d; absence of HAp). Homogenization of the dichloromethane solution of PS-CH₃ and the aqueous dispersion of HAp nanoparticles (Figure 3e) also failed to produce a stable emulsion. From these results, it was confirmed that interaction between HAp particles in the aqueous phase and carboxyl groups in oil phase is a driving force for HAp nanoparticles to adsorb to the oil–water interface and plays an important role in forming stable emulsions.

The dichloromethane droplets were spherical and fairly polydisperse (see Supporting Information Figure S4). The number-average diameters of emulsion droplets were measured from the micrographs, and the effect of PS-COOH concentration in dichloromethane on droplet size was determined (Figure 4a). At concentrations greater than 1 wt % polymer, droplet size increased with polymer concentration, due to a significant increase in the viscosity of the polymer solution (Figure 4b). At concentrations less than 1 wt %, a higher concentration led to a smaller droplet size, and smaller droplets were obtained by dissolving lower-molecular-weight PS-COOH at all concentrations. These results indicate that the amount of COOH end groups played a critical role in

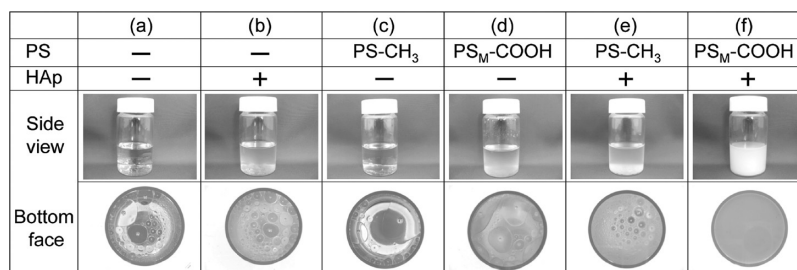


Figure 3. Digital photographs of dichloromethane/water mixtures prepared under different conditions. Images were obtained immediately after mixing. Polymer, 1.0 wt % in dichloromethane; HAp nanoparticles, 0.04 wt % in water; oil/water, 1/10 (w/w).

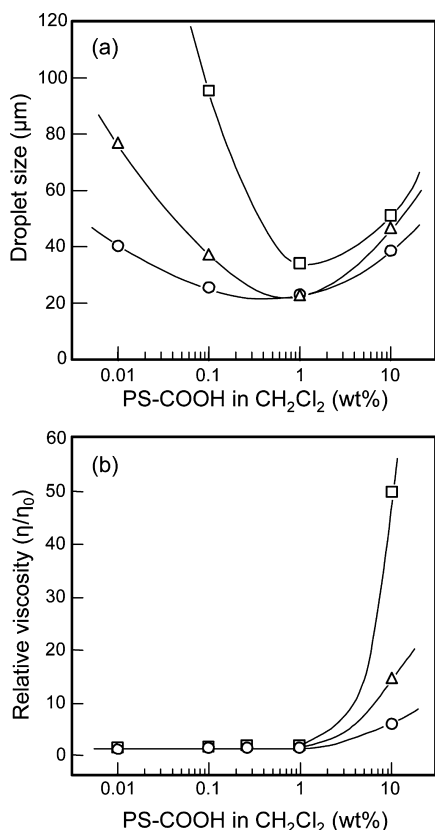


Figure 4. Variations of (a) the size of HAp nanoparticle-stabilized dichloromethane droplets (HAp nanoparticles, 0.04 wt % in water; oil/water, 1/10 (w/w)) and (b) the relative viscosity of dichloromethane solution dissolving (□) PS_H-COOH, (△) PS_M-COOH, and (○) PS_L-COOH as a function of polymer concentration.

determining droplet diameter. At a polymer concentration of 0.1 wt %, occupied areas of COOH groups on the droplet surface were 64 Å²/molecule for PS_H-COOH ($M_n = 16\,400$; droplet diameter, $96 \pm 34\ \mu\text{m}$), 21 Å²/molecule for PS_M-COOH ($M_n = 2200$; droplet diameter, $38 \pm 10\ \mu\text{m}$), and 11 Å²/molecule for PS_L-COOH ($M_n = 800$; droplet diameter, $26 \pm 9\ \mu\text{m}$) under the assumption that all COOH groups were located on the droplet surfaces. Hence, the interaction between PS-COOH and the HAp nanoparticles at the oil/water interface should be greater for lower-molecular-weight PS-COOH.

Microsphere Formation by Solvent Evaporation. After evaporation of dichloromethane from the HAp nanoparticle-stabilized emulsion, HAp nanoparticle-coated microspheres were obtained as shown in Figure 5. A gas chromatographic study could detect no residual dichloromethane (<10 ppm) in

any dispersion after evaporation for 24 h at room temperature (ca. 20 °C). For PS_H-COOH, the number-average diameter of the droplets decreased from 34 to 7 μm (volume reduction, 99.1%), and spherical morphology was maintained after evaporation (Figure 5a). The SEM observations revealed that free HAp nanoparticles not adsorbed on the microsphere surfaces were present among the microspheres (Figure 5d-1 and d-2), and microsphere surfaces were not completely covered by HAp nanoparticles (Figure 5d-2 and d-3). For PS_M-COOH, the number-average diameter of the droplets decreased from 23 to 4 μm (volume reduction, 99.5%), and the spherical morphology also was maintained after evaporation (Figure 5b). SEM observations revealed that free HAp nanoparticles were present among the microspheres (Figure 5e-1 and e-2), but most microsphere surfaces were completely covered by HAp nanoparticles (Figure 5e-2 and e-3). The difference in the area of HAp covered should be due to the differences in surface concentrations of COOH groups. In the case of the lowest molecular weight PS_L-COOH, the spherical oil droplets were deflated after evaporation (Figure 5c; see also Supporting Information Figure S5 showing in situ deformation in the aqueous medium). The SEM observations revealed that few free HAp nanoparticles were present (Figure 5f-1 and f-2), indicating that most of the nanoparticles were adsorbed on the microsphere surfaces. The TG analysis (conducted after removal of free HAp nanoparticles not adsorbed on microsphere surfaces) also indicated that the number of HAp nanoparticles on microsphere surfaces increased with a decrease in molecular weight of PS-COOH (see Supporting Information Figures S6 and S7: HAp, 9.5 wt % for PS_H-COOH; HAp, 19.4 wt % for PS_M-COOH; HAp, 24.4 wt % for PS_L-COOH). Note that the deformation of the PS_L-COOH microspheres was not due to the nature of PS_L-COOH because spherical microspheres were obtained by evaporation of dichloromethane from sodium dodecyl sulfate (SDS)-stabilized droplets containing PS_L-COOH (see Supporting Information Figure S8). The SDS molecules can desorb from liquid/liquid interfaces,²⁷ which should lead to the shrinkage of spherical microspheres with the interfacial area decreasing (due to interfacial tension between oil and water) along with dichloromethane evaporation. Hence, HAp nanoparticles (and strong adsorption of nanoparticles onto the oil surface) are necessary for deformation of the microspheres.

Asekomhe et al. studied the behavior of a macroscopic water drop (~3 mm diameter) hanging from a capillary tube and covered with silica particles (13 μm diameter) suspended in an oil phase. They observed that the interface containing suitable hydrophobic particles crumpled upon significant reduction of the water droplet volume²⁸ because the particles remained attached to the oil–water interface due to their biwettable

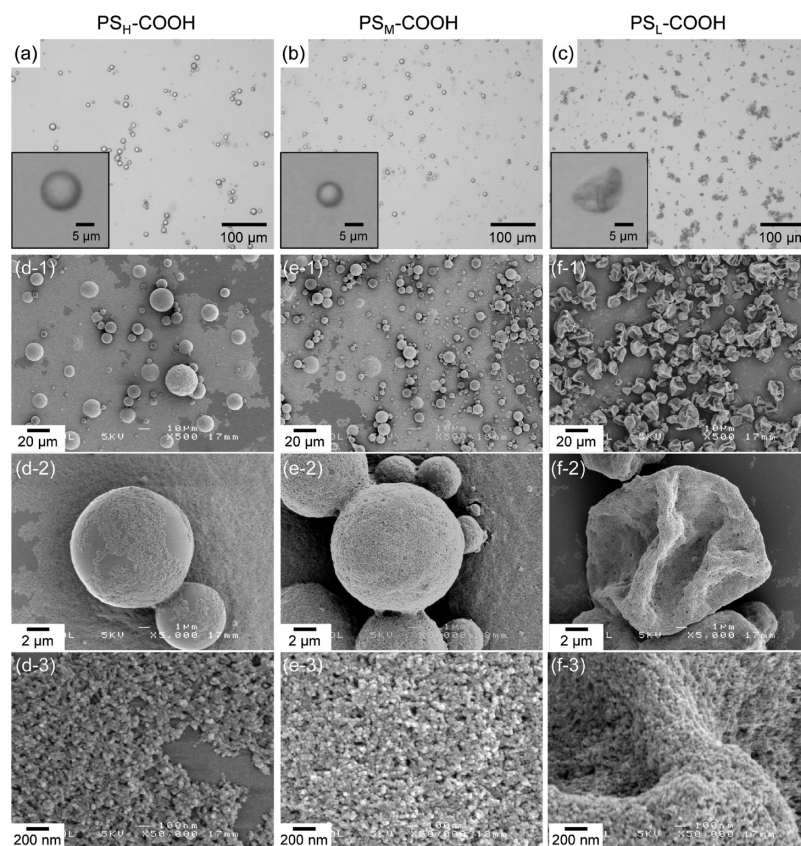


Figure 5. (a–c) Optical micrographs and (d–f) SEM photographs of HAp nanoparticle-coated PS microspheres prepared from the emulsions containing (a,d) PS_H -COOH, (b,e) PS_M -COOH, and (c,f) PS_L -COOH, observed at different magnifications. PS-COOH, 1.0 wt % in dichloromethane; HAp nanoparticles, 0.04 wt % in water; oil/water, 1/10 (w/w).

nature, even under significant drop deformation. With hydrophilic particles, the droplet appeared to deform with very little crumpling. Datta et al. studied the structural transitions of nanoparticle-stabilized droplets (ethylene glycol/glycerol as a dispersed phase; chlorobenzene as a continuous phase; hydrophobic, 15 nm silica as a particulate emulsifier) as their volumes were reduced.²⁹ They found that droplets deformed (buckled or crumpled) upon addition of an unsaturated continuous phase in the emulsion, and the resulting morphology depended on both the extent of volume reduction and the average droplet size. Results from the present study and previous reports suggest that deformation of droplets/microspheres is influenced by the extent of the interaction between nanoparticles and polymer at the interface (Figure 6). For example, when weak interactions are involved (i.e., PS_H -COOH) and nanoparticles can desorb from the interface, microspheres shrink while maintaining a spherical form due to interfacial tension. In contrast, when strong interactions prevent nanoparticles from desorbing from the interface, microspheres must deflate to maintain the interfacial area.

Microsphere Formation by Suspension Polymerization. HAp has been also used as a Pickering stabilizer for suspension polymerization of styrene in the polymer industry, but always along with conventional water-soluble surfactants (such as SDS and sodium dodecylbenzenesulfonate) or polymeric stabilizers [such as poly(vinylpyrrolidone)].³⁰ The present study confirmed that HAp nanoparticles alone could not function as a particulate emulsifier for styrene monomer droplets; however, styrene monomer droplets were successfully

stabilized with the aid of PS-COOH dissolved in the monomer phase without the use of water-soluble surfactants/stabilizers (data omitted). After polymerization with AIBN initiator at 65 °C for 12 h (conversion, 94%), spherical PS microspheres ($76 \pm 35 \mu\text{m}$) were obtained with surfaces uniformly coated with HAp nanoparticles, as shown in Figure 7. Note that the outer surfaces of the nanoparticles covering the microspheres display a pure HAp surface due to the absence of surface modifiers in the aqueous (continuous) phase.

4. CONCLUSIONS

We have clearly demonstrated that the interactions between end groups of polymers dissolved in an oil (dispersed) phase and nanoparticles in an aqueous (continuous) phase at the oil–water interface play important roles in stabilizing Pickering-type emulsions and in controlling the morphology of nanocomposite microspheres prepared by evaporating solvent from the emulsion. We have also achieved HAp-stabilized suspension polymerization without water-soluble surfactants/stabilizers. The surface of the microsphere was covered with particulate emulsifiers, which are expected to have a pristine surface exposed to the continuous aqueous phase, because the particulate emulsifier was used without any surface-active modification and no surface-active molecules were added. Although this study focused on HAp nanoparticles as the particulate emulsifier and carboxylated PS as the polymer, these novel findings extend the applicability of Pickering-type emulsions and nanocomposite microspheres, and will be also useful to synthesize Janus particles efficiently by modifying the particulate emulsifiers on composite microspheres.

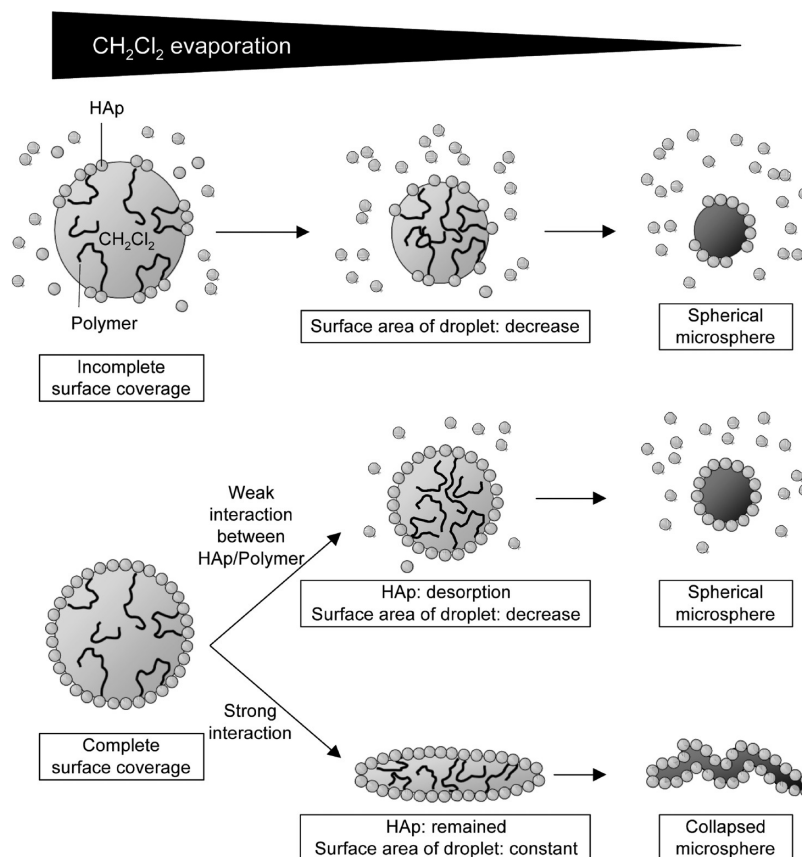


Figure 6. Schematic representation of morphological changes of the droplets/microspheres during dichloromethane evaporation. The strength of the interaction between polymer and HAp is influenced by the polymer structure (end groups and molecular weight) and the polymer concentration.

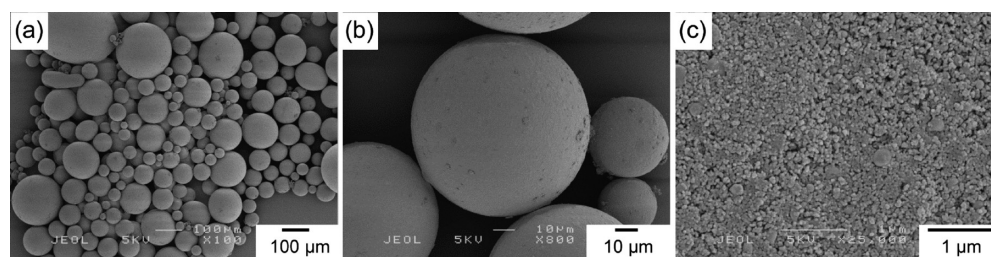


Figure 7. SEM photographs of HAp-coated PS microspheres prepared by suspension polymerization for styrene monomer droplets stabilized with HAp nanoparticles dispersed in the aqueous medium and $\text{PS}_L\text{-COOH}$ dissolved in the monomer droplets. $\text{PS}_L\text{-COOH}$, 1.0 wt % in styrene; HAp nanoparticles, 0.33 wt % in water; oil/water = 1/10 (w/w). Magnifications: (a) 100, (b) 800, and (c) 25 000.

■ ASSOCIATED CONTENT

Supporting Information

Additional figures and table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by the R&D of Nanodevices for Practical Utilization of Nanotechnology of the New Energy and Industrial Technology Development Organization (NEDO), a Grant-in-Aid for Scientific Research on Innovative Areas “Molecular Soft-Interface Science” from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP) from the Japan Science and Technology Agency (JST).

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