Preparation of Nearly Monodispersed Polystyrene Particles Formed by Polymerization in a Surfactant-free Emulsion with Silica Particles

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When the polymerization of styrene with a lipophilic initiator was conducted in an O/W emulsion, which was stabilized by unmodified monodispersed silica particles, it was found that near monodisperse polystyrene particles with different submicrometer size were formed in the emulsion. After the polymerization, the solution of silica and polystyrene mixed particles was obviously more stable than the silica-dispersed solution.

Monodispersed particles with various sizes are the focus of much attention on account of their use as the building blocks of hierarchical nanostructures.[1–3] The control of size and distribution, surface modification, and the construction of two-dimensional and three-dimensional arrays of monodispersed particles, have all been researched intensively.[1–3] As inorganic monodispersed particles, silica beads prepared by the Stober method,[4] a technique based on the sol–gel method, have proved very popular. Polymer particles are often prepared by polymerization in microemulsions and emulsions,[5] in which a monomer droplet is formed in the presence of surfactants. Recently, soap-free polymerization[6] has become popular as a technique for the preparation of monodispersed polystyrene particles with charged surfaces.

In fact, emulsions have also been prepared with solid particles instead of regular molecular surfactants. This fact has been known since the early 1900s, and this type of emulsion is categorized as a surfactant-free emulsion.[7] Binks and Lumsdon[8,9] demonstrated that the structures of emulsions stabilized by hydrophobic monodispersed silica particles were able to control not only W/O type, but also O/W type emulsions as a function of the salt concentration, in the same way that regular emulsions with molecular surfactants do. We report here the polymerization of styrene using a lipophilic initiator in an O/W emulsion stabilized by unmodified monodispersed silica particles under static condition without suspension. Surprisingly, it was found that near monodisperse polystyrene particles were formed in the emulsion.

Nearly monodispersed silica particles (average diameter 530 nm, $Dw/Dn = 1.13$, z potential -34.2 mV at pH 7), synthesized according to the sol–gel method, were used to prepare an emulsion. Styrene was suspended in aqueous solution with 1 wt% silica particles. In the emulsion, the concentration of styrene was approximately 8.8% v/v. After the addition of AIBN as an initiator and the elimination of oxygen, the polymerization reaction was conducted for 24 h at 60 °C statically without mixing the two phase solution consisting of an OW emulsion (lower phase) and excess styrene (upper phase). After the polymerization, the upper styrene phase was fully polymerized as confirmed by the formation of transparent bulk block. In the emulsion phase, a dense milky suspension was formed.

Figure 1 shows SEM images of the template silica particles (a) and mixed particles prepared by the polymerization of a silica-stabilized styrene O/W emulsion (b). It was found that PS particles with 200 nm average diameter newly formed by polymerization were observed in silica particle solutions with high reproducibility. The template silica particles and the PS particles were spontaneously separated during the casting process, although the mixed particles were dispersed homogeneously. This indicates that there is essentially no strong interaction between either set of particles. In addition, the silica surface seems to be spared from polystyrene modification. Thermogravimetric (TG) measurements of the polymerized emulsion moieties after drying revealed that the weight ratio of PS and silica was typically 59 and 41% in terms of the thermal decomposition of PS at 300 °C. The PS ratio was higher than that expected from the styrene concentration in the emulsion, indicating that styrene for polymerization was also supplied from the upper styrene phase. The removal of silica particles were conducted by silica dissolution in potassium hydroxide solution and the resulting solutions were purified by 4 times centrifugation/redispersion cycles with pure water. After the treatment, only small particles with 200 nm average diameter were obtained from the solution, as shown in Figure 1c. This also confirmed the formation of small polystyrene particles by polymerization in a monodispersed silica-stabilized O/W emulsion.

The results of the SEM observations were confirmed by size distribution measurements performed using the dynamic laser

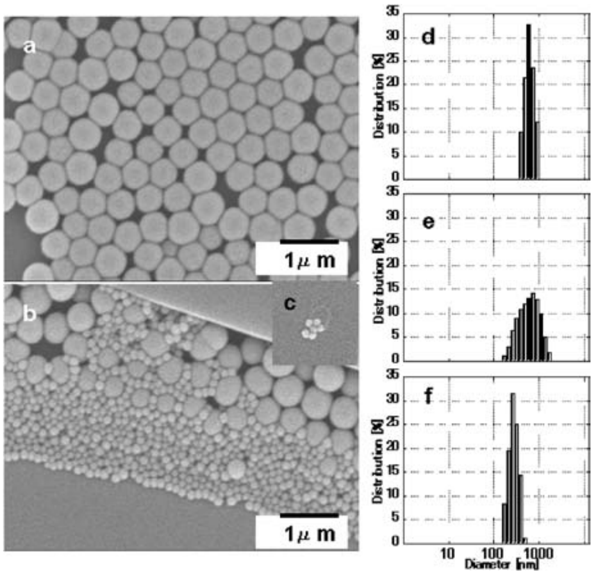

Figure 1. SEM images (a)–(c) and size distributions (d)–(f) of template silica particles (a) and (d), silica/PS mixed particles after polymerization (b) and (e), and PS particles after alkali treatment to remove the silica particles (c) and (f).

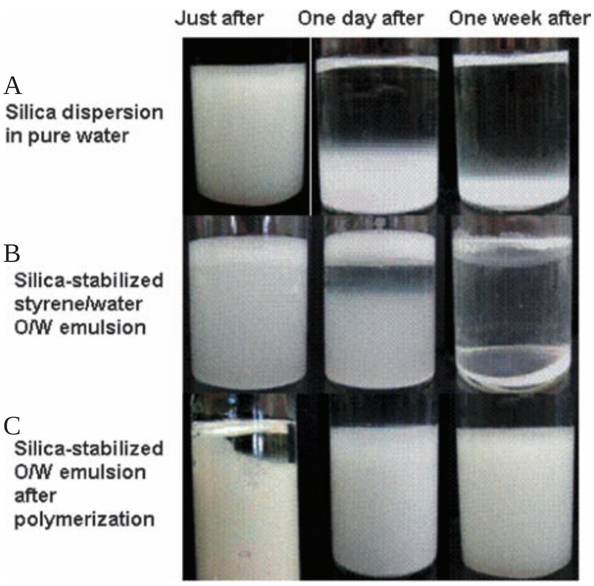

Figure 2. Time-dependent emulsion stabilities for a silica dispersion in pure water (upper column), a silica-stabilized styrene/water O/W emulsion (middle column) and a silica-stabilized O/W emulsion after polymerization (lower column).

scattering method. The size distribution histogram of template silica shows a relatively narrow distribution of silica particles (Figure 1d). In contrast, the histogram of the silica/PS mixed particle dispersed solution indicated a mixture of particles with a wide distribution of 598 ± 306 nm (Figure 1e). In the particle solution after the alkali treatment, the distribution moiety with large size (350–650 nm) attributed to template silica was noticeably absent, and only the distribution moiety with small size (249 ± 62 nm) attributed to PS particles remained (Figure 1f). These results clearly indicate that the solution after polymerization was a mixture of silica particles and half-sized PS particles. Certainly, the distribution of silica/PS mixed solutions might be a simple addition of those of template silica and the newly formed PS particles. The PS particles prepared by polymerization had a narrow dispersity with an average diameter 250 nm ($Dw/Dn = 1.14$). Rarely, a small amount of larger sized species (500–600 nm) was observed in the histogram. This is likely attributed to the aggregated PS particles, as aggregations were frequently observed in the SEM images of PS samples after alkali treatment. The PS particles obtained after the alkali treatment could be dispersed into water with few precipitates, which might be due to the weak negatively charged surface of the PS particles originated from AIBN.

Figure 2 shows the dispersion stability of the silica/PS mixed particle dispersed solution. Interestingly, the emulsion stability after polymerization was reproducibly more stable than that before polymerization. In the case of the silica-dispersed aqueous solution without salt or surfactant, and the unpolymerized emulsion, the emulsion easily breaks just one day after preparation, as shown in Figures 2A and 2B, respectively. The emulsion and the silica-dispersed water solution were homogeneously stable for at least several hours. In contrast, the silica/PS mixed solution after polymerization was drastically stable, as shown in Figure 2C. A homogeneous milky polymerized emulsion was stably observed and no sedimentation was observed, even after several weeks (Figure 2C). The typical z potentials of template silica in pure water, the silica/PS mixture and PS were -34.2, -28.6, and -27.8 mV, respectively. After polymerization, the z potential was not changed, because there was no other charged species. Note that the polymerization was conducted with a lipophilic initiator, AIBN, rather than a hydrophilic initiator. When a hydrophilic anionic initiator, Potassium peroxodisulfate (KPS), was applied to the polymerization reaction in the same emulsion, polydispersed PS particles were formed.

Among various reports about organic–inorganic hybrid particle systems, the comparison between our results and the results obtained by Schmid and co-workers[10] might be interesting, because of the similarity in terms of particle formation. Schmid and co-workers reported that the suspension polymerization of styrene in alcoholic solution with monodispersed silica (several ten nm in diameter) sol initiated by a lipophilic initiator lead to the formation of PS particles incorporated with silica. The surface of the formed polystyrene particles (1 micron in diameter) was partially covered with tiny silica particles. The surface charge of the silica on the PS particles gave the impression of an ability to achieve good dispersibility by electrostatic repulsion. However, in our system, the silica particles and PS particles might be independently isolated. The bigger silica particles were not incorporated into the formed PS particles. By elementary analysis, the purity of PS was more than 98% after alkali treatment. Furthermore, the silica particles might not be modified by PS, as no change in the z potential was observed after polymerization.

The polymerization would occur in the emulsion solution phase, rather than on the surface of silica, because of the fact that there is no strong interaction between the silica template particles and PS particles. The near monodispersity of the PS particles is likely due to the constant slow supply of monomer from the emulsion solution phase. Abe and co-workers reported that the dispersion stability of surfactant-free O/W emulsions with the addition of hydrophobic polymers was improved.[11] This result might suggest that the formed PS polymers and silica emulsion stabilize each other in the system.

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