Research Article

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Silica/polymer core–shell particles prepared via soap-free emulsion polymerization

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Abstract: In this study, core–shell particles were prepared as a hybrid material, in which a thin polymer shell was formed on the surface of the SiO₂ sphere particles. The core–shell structure was successfully achieved without adding a surfactant via simple free-radical polymerization (soap-free emulsion polymerization) for various monomers of styrene, methyl methacrylate (MMA), and their derivatives. MMA formed thin homogeneous shells of polymer (PMMA) less than 100 nm in thickness with complete surface coverage and a very smooth shell surface. The obtained shell morphology strongly depended on the monomers, which suggests different shell formation mechanisms with respect to the monomers. It was found that the cross-linking monomer 1,4-divinylbenzene tends to promote shell formation, and the cross-linking reaction may stabilize the core–shell structure throughout radical polymerization. It should also be noted that the present method produced a considerable amount of pure polymer besides the core–shell particles. The glass transition temperatures of the obtained polymer shells were higher than those of the corresponding bulk materials. This result suggests strong interactions at the core–shell interface.

Keywords: soap-free polymerization, core–shell particles, silica, glass transition, cross-link

1 Introduction

Hybrid nanoparticles composed of inorganic and organic materials have been attracting immense attention and

can contribute to the development of various composite materials. Numerous studies have attempted to manufacture core–shell particles with a polymeric shell and an inorganic core (1). Such composite particles can be used as fillers for nanocomposites, where the filler reinforces the matrix resin because of its excellent compatibility with the matrix (2–6). Other potential applications for core–shell particles are electronics (7–10), pharmaceutical materials (11,12), optics (13), and catalysis (14–17). Various methods have been developed to prepare the core–shell particles (1,15,18–22). Among them, emulsion or suspension polymerization is the most common technique used to prepare the inorganic/polymeric core–shell particles, where the radical polymerization is performed in the presence of suspended core particles in water (23–30). The suspension (or emulsion) polymerization technique can also be applied to prepare whisker-shaped core–shell and hollow particles using CaCO₃ core particles (31–34).

To stabilize the suspended droplets of monomer and core particles in water, amphiphilic surfactants are often used. However, in general, it is difficult to remove the surfactant completely after polymerization (1). The residual surfactant may significantly affect the properties of the obtained nanomaterials, such as the glass transition temperature (35). Therefore, developing a technique to obtain core–shell particles without using any surfactants is essential to elucidate the nano-size effects on their physical and thermal properties.

In this study, core–shell particles were prepared using spherical silica particles as cores. Emulsion polymerization with an aqueous initiator without a surfactant (soap-free polymerization) was performed for various monomers of styrene, methyl methacrylate (MMA), and their derivatives to obtain polymer layers that cover the surface of the silica cores. The polymerization conditions were optimized for each monomer to successfully achieve a core–shell architecture. The glass transition temperature T_g of the obtained polymer shells was investigated via the differential scanning calorimetry (DSC), and the results were compared with the corresponding bulk T_g .

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2 Experimental

Silica nanoparticles with diameters of 300, 500, and 1,000 nm (KE-S30, KE-S50, and KE-S100; Nippon Shokubai, Osaka Japan) were used as core materials. MMA, 2-hydroxyethyl methacrylate (HEMA), styrene (S), 4-chlorostyrene (ClS), 4-methoxystyrene (MOS), 4-methylstyrene (MS), and the cross-linking reagent 1,4-divinylbenzene (DVB) were distilled under reduced pressure before use. The surfaces of the silica particles were modified with a silane coupling reagent, 3-(trimethoxysilyl)propyl methacrylate (MAPTMS), which was used as received. It was found that the SiO₂ particles with no surface treatment did not successfully yield core-shell particles (36). The surface modification of the silica particles was performed as follows: 90 ml of ethanol and 1.0 ml of MAPTMS were added to 10 g of silica particles suspended in 90 ml of pure water. Then, acetic acid was added until the pH became 4.0. The obtained weakly acidic suspension was stirred for 30 min at 25°C and sonicated for 3.5 h. The mixture was stirred again for 24 h at 25°C. The suspended particles were precipitated via centrifugation at 2,000 rpm for 8 min, and the precipitated particles were soaked in methanol for neutralization. The precipitates were dried in air at 25°C. The obtained powder-like material (surface-modified SiO₂ particles) is referred to as SiO₂-MAPTMS henceforth. The modification with MAPTMS was confirmed using X-ray photoelectron spectroscopy (JPS-9010MCY; Jeol, Akishima, Japan) from a signal of the C=C bond on the surface of the modified silica.

The polymer/SiO₂-MAPTMS core-shell particles were prepared via soap-free emulsion polymerization. Sodium peroxodisulfate or potassium peroxodisulfate was used as an initiator, and the aforementioned monomers were polymerized. In some cases, the cross-linking reagent DVB was included in the polymerization reaction (random copolymerization). All these monomers were distilled under reduced pressure before use. Polymerization was performed under a nitrogen atmosphere at a constant temperature

(40, 60, or 80°C). Various recipes with respect to the amount of each reagent were tried to yield core-shell particles successfully. The optimized conditions that were found by trial and error are listed in Table 1.

The morphology of the obtained particles was investigated via transmission electron microscopy (TEM) using a Jeol JEM-2000FXII operated at an acceleration voltage of 200 kV. The sample was dispersed and diluted in methanol, and it was deposited onto a microgrid covered with a carbon-coated nitrocellulose membrane. The glass transition behaviors of the polymer shells were investigated using a DSC (Pyris Diamond, Perkin Elmer). The temperature and heat flow were calibrated using an indium standard, and the measurements were conducted under a nitrogen atmosphere. The step-scan heating mode, which is a type of temperature-modulated DSC, was used to yield nonreversing heat flow and reversing heat capacity. Scans were performed with a temperature step of 2 K at a heating rate of 5 K min⁻¹ and a holding time of 1.5 min. As the prepared core-shell particles often contained only small fractions of polymer, their *T_g* signal tended to be rather weak. To emphasize the weak *T_g* signal, the samples were annealed below the bulk *T_g* (*T_g*^{bulk} – 30°C) for 72 h before the DSC scan. Then, the *T_g* of the polymer shell was evaluated from the signal of the enthalpy overshoot that appeared in the nonreversing heat flow trace.

To evaluate the bulk values of *T_g*, the polymer samples were synthesized under the exact same conditions in the absence of the core particles. The obtained polymers were separated in methanol and then dissolved in toluene, followed by precipitation in methanol (or *n*-hexane). The bulk reference samples thus obtained were dried under vacuum at room temperature for 24 h. The molar mass of PMMA (non-cross-linked) was also determined for the bulk reference samples prepared above via gel permeation chromatography with three polystyrene (PS) gel columns (TSK gel G-MHHR-M)

Table 1: Optimized conditions for emulsion polymerization

Polymer	Temperature (°C)	Monomer (M)	Initiator (10 ⁻³ M)	Diameter of core (nm)	DVB (10 ⁻³ M)
PMMA (a)	80	0.41	4.18	1,000	0
PMMA (b)	80	0.41	40	500	0
PMMA (c)	80	0.115	100	500	0
PCIS	60	0.19	4.18	300	7.9
PMS	80	0.17	4.18	300	4.0
PMOS	80	0.17	4.18	300	4.0
PHEMA	40	0.18	4.18	300	7.9
PS with no cross-linker	80	0.87	9.41	1,000	0
PS with a cross-linker	60	0.19	4.18	300	7.9

connected to a Waters Alliance e22695 (Tokyo, Japan). To evaluate the polymer content in the obtained core-shell samples, the thermogravimetric analysis was performed using a thermogravimetric analyzer (DTG-60; Shimadzu, Kyoto, Japan).

3 Results and discussion

Figure 1 shows the TEM images of the PMMA/SiO₂-MAPTMS core-shell particles prepared via emulsion

polymerization under three different conditions. Core-shell particles were successfully obtained for PMMA shells with no cross-linking reagent. The surface of the PMMA shell was rather smooth, and the shell thickness was homogeneous, especially for PMMA (a). This may be due to the compatibility of MMA with the silica surface. The surface of the silica particles used in this study is considered to be slightly hydrophilic even after modification with MAPTMS; therefore, it is compatible with MMA. In the suspended state before polymerization, the surface of the SiO₂-MAPTMS particles was possibly covered with a thin monomer layer. It is likely

Figure 1: TEM images of the PMMA/SiO₂-MAPTMS core-shell particles prepared under three conditions: PMMA (a), PMMA (b), and PMMA (c), as shown in Table 1.

that at first the initiator reacted with MMA in the aqueous phase, then it migrated into the monomer phase around the core (8,37). In addition, it was found that a considerable amount of pure PMMA besides the shell part was produced. Comparison of the result of the thermogravimetric analysis and the average shell thickness obtained through the TEM revealed that the mass ratio of the shell to the total mass of PMMA ranged from 30 to 37%. The formation of pure polymer originates from the mechanism of emulsion polymerization, where the initiation reaction occurs in the aqueous phase. Thus, our method of polymerization has a disadvantage that it produces core-shell particles only partially, although well-defined homogeneous core-shell structures can be easily obtained. On the other hand, TEM observation revealed nearly 100% of surface coverage of the core by the polymer shell.

Such a core-shell structure is rather stable during polymerization because of the high compatibility. It was found that the shell thickness depends weakly on the amount of monomer fed. The shell of PMMA (a) exhibited the most homogeneous morphology with a thickness of 42 nm. As for PMMA (b), the shell thickness showed a distribution that ranged from 37 to 52 nm. The molar mass of the shell of PMMA (b) was determined to be $M_n = 26,400$ Da and $M_w = 36,400$ Da and for PMMA (c), $M_n = 19,900$ Da and $M_w = 24,500$ Da.

For the monomers of styrene derivatives, a core-shell structure was obtained when a cross-linking monomer (DVB) was added. Figure 2 shows PCIS/SiO₂-MAPTMS core-shell particles, where the PCIS shell was cross-linked with DVB. Thicker shells up to 140 nm were obtained. In addition, pure PCIS spheres without a core were simultaneously obtained, but most of the core particles were covered with the polymer shell as in the case of PMMA. Shell formation was not observed if

polymerization was performed without the cross-linker. This was also the case for PMS and PMOS. Cross-linking may stabilize the shell structure during polymerization in aqueous suspensions of the core particles, as was reported in studies on calcium carbonate cores (31,32). Furthermore, gaps between the core and the shell occurred occasionally, as indicated by the arrow in Figure 2 (left panel). This suggests that no chemical (covalent) linkage was formed between MAPTMS and PCIS in the areas of the gaps because of low affinity of CIS with the core surface compared with that of MMA. The mechanism of the gap formation may be related to the difference in thermal shrinkage between the core and the shell on cooling after polymerization. The gap between the core and the shell tends to form when the shell thickness is relatively large. The gap also formed for PMOS and PMS, of which the shells are thicker than that of PCIS, as shown below. In contrast, for PMMA and PHEMA, which exhibited thinner shells, no gap was observed.

Figure 3 shows the TEM images of the PMOS/SiO₂-MAPTMS particles with cross-linked shells. Here, very thick outer shells are observed. Interestingly, the cores were not necessarily located at the center of the particles, and the entire shape of the particles was ellipsoidal in general. The thickness of the PMOS shell ranged rather widely (140–500 nm). These morphological features are similar to those of the particles with PS shells prepared using different methods (9,10). Figure 4 shows PMS/SiO₂-MAPTMS particles with cross-linked shells. The features of the core-shell structure are similar to those of the PMOS/SiO₂-MAPTMS particles. Similar to the PMOS shell, the thickness of the PMS shell was also in a wide range (140–400 nm). It is noted again that the gaps between the core and the shell partially occur for some particles. The morphological similarity

Figure 2: TEM images of the PCIS/SiO₂-MAPTMS core-shell particles. The polymer shell was cross-linked with DVB. The white arrow in the left panel indicates the gap between the core and the shell.

Figure 3: TEM images of the PMOS/SiO₂-MAPTMS core-shell particles. The polymer shell was cross-linked with DVB.

Figure 4: TEM images of the PMS/SiO₂-MAPTMS core-shell particles. The polymer shell was cross-linked with DVB.

between the PMOS and the PMS shells may originate from their similar chemical nature. It was also found that almost all the core particles were covered with the polymer for both PMOS and PMS.

Figure 5 shows the TEM images of the PS/SiO₂-MAPTMS composite particles. When the cross-linker DVB was not included, many small PS spheres were obtained, which were attached to the surface of the core particles. This resulted in a flower-like morphology (Figure 5a). The morphology suggests that the small PS particles formed separately from small monomer droplets suspended in water and then migrated and attached to the surface of the cores. The diameter of these PS particles ranged from 90 to 280 nm. In addition, the surface of the core was not completely covered with the PS particles, as shown in the right image of Figure 5a. In contrast, thick and ragged shells formed when the cross-linker was included in the polymerization, as shown in Figure 5b. However, the obtained shells were thicker but less homogeneous than those in PMMA, and the surface coverage was incomplete. Some of the particles still appeared to be flower-like, suggesting the same mechanism of shell formation as in the case of non-cross-linked shells (Figure 5a). The results for PS

suggest that the compatibility of the monomer (styrene) with the core surface is lower than that of the monomers exhibiting thicker shells, as shown in Figures 2–4 (chlorostyrene, methylstyrene, and methoxystyrene). It is likely that for the monomers with thicker shells, a monomer layer formed on the core surface prior to the commencement of polymerization because of their higher compatibility with the core. Core-shell particles with very thick PS shells have been reported to form successfully via emulsion polymerization when an aqueous monomer (styrene sulfonate sodium salt) was included (9,10). Such an aqueous monomer that is highly compatible with SiO₂ may promote the formation of a homogeneous monomer layer on the core surface during polymerization.

A hydrophilic monomer, HEMA with the cross-linker DVB (Table 1), was also investigated. The obtained TEM images are presented in Figure 6, where very thin shells of PHEMA are observed on the core particles. The surface of the shell appeared to be ragged compared with that of PMMA. The average shell thickness was determined to be 7.3 nm. No gap was observed between the core and the shell; this suggests that the shell was covalently bonded through the silane coupling reagent

Figure 5: TEM images of the PS/SiO₂-MAPTMS particles for (a) PS polymerized with no cross-linker and (b) PS polymerized with a cross-linker DVB.

to the core surface. Nearly 100% surface coverage was achieved, which suggests high affinity of the monomer because of its hydrophilic nature. The mass ratio of the shell to the total mass of PHEMA was evaluated to be 17%.

For the polymer shells, the thermal properties were investigated via the DSC measurements and their T_g was evaluated. Table 2 shows the results with the average shell thickness. In general, the T_g 's of the polymer shells were higher than the corresponding bulk values.

Note that T_g^{bulk} reported in this table is for polymers with the same degree of cross-linking in a bulk state. The increase in T_g may be due to the strong interactions at the core-shell interface, where the polymer chains have limited mobility owing to the binding at the interface. MAPTMS may play a role in decreasing the polymer mobility at the interface. PCIS/SiO₂-MAPTMS exhibited partial gaps at the core-shell interface, but they still showed a higher T_g than the bulk value. The increase in T_g for PCIS may be partially attributed to the heterogeneous distribution

Figure 6: TEM images of the PHEMA/SiO₂-MAPTMS particles. The polymer shell was cross-linked with DVB.

Table 2: Average shell thickness d and the glass transition temperature T_g of the shells

Polymer	d (nm)	T_g (°C)	T_g^{bulk} (°C)
PMMA (a)	42	140	127
PMMA (b)	37–52	127	123
PMMA (c)	100	123	114
PCIS	140	145	140
PHEMA	7.3	115	100
PS with a cross-linker	20–90	137	130

of cross-linking points in the shell; a similar phenomenon of T_g enhancement was reported previously for the cross-linked polymer shells in other core-shell systems (31,32). In addition, it should be noted that the prepared samples contained polymer particles without a core (polymer spheres and/or larger bulk-like entities of pure polymer), which affected the observed T_g . Nevertheless, the general trend of increase in T_g for the core-shell particles is assured because the pure polymer particles with bulk-like nature do not contribute to the increase in T_g , although quantitative discussion with respect to the shell thickness could not be made.

4 Conclusions

In this study, the SiO_2 /polymer composite particles with core-shell structures were successfully synthesized via soap-free emulsion polymerization. The obtained morphology strongly depended on the monomer used, which determined the mechanism of the radical polymerization. PMMA showed homogeneous shells with rather smooth shell surfaces. This may be a result of the compatibility of MMA with the silica surface modified with MAPTMS. The shells of PMS, PMOS, and PCIS were also obtained if the cross-linking monomer DVB was copolymerized. The shells of these polymers were much thicker than those of PMMA. For non-cross-linked PS, small polymer spheres were aggregated on the silica surface to form a flower-like structure. The cross-linked PS shells were still less homogeneous than those of PMMA. These results may originate from the low compatibility of styrene with the core surface. This low compatibility may prevent the formation of a monomer layer on the core surface in a suspended state prior to polymerization. Very thin shells were successfully obtained for PHEMA, although the shell surface was ragged. The glass transition temperature of the obtained

shells was found to be higher than the corresponding bulk value for all the polymers investigated. This finding indicates that the interaction at the core-shell interface is essential in determining the physical properties of the composite materials with nano-sized geometries.

It should be noted that the present method of soap-free emulsion polymerization produces a considerable fraction of pure polymer besides the core-shell particles. The fraction of pure polymer may be reduced by improving the preparation procedures. In addition, separation of the core-shell particles from the pure polymer may be possible by centrifugation of the as-polymerized suspension.

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