## Efficient Production of Block-copolymer-coated Ceramic Nanoparticles by Sequential Reversible Addition–Fragmentation Chain-transfer Polymerizations with Particles (SqRAFTwP)

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Ceramic nanoparticles (NPs) were surface modified and dispersed by in situ synthesized block copolymers. Living radical polymerization with sequential addition of monomers enables the effective coating of ceramic NPs by block copolymers. The method enables us to add stable polymer layers on any kind of NPs; therefore, it can help the mass production of polymer-coated inorganic NPs and drastically reduce the cost, without sacrificing their performance.

Composite materials, especially composites of inorganic materials and polymers, are very attractive because they can exhibit promising new properties that have been believed to be trade-off functions.<sup>1</sup> In order to solve the trade-off, stable dispersions of filler nanoparticles (NPs) in a polymer matrix has to be achieved. Polymer grafting to the surface of inorganic materials is promising.<sup>2–6</sup> Because polymeric materials are in a metastable state in most cases, composite materials of just blended polymers and inorganic materials are not stable, i.e., they will segregate from each other. When the inorganic NPs have grafted polymer chains, segregation will be inhibited because the same polymer material can be miscible.

Many studies of grafting polymer chains on NPs have been reported. Some of the studies proved the advantage of polymer grafting on dispersions of inorganic NPs in polymer matrixes. Polymer grafting is effective, but all of the polymer grafting methods need anchoring reagents to connect inorganic surfaces and polymers.<sup>3–7</sup> Recently, I proposed a method for the direct production of polymer-grafted ceramic NPs without using anchor and/or linker reagents.<sup>2</sup> This technique drastically increases the combinations of ceramics and polymers that can be grafted and reduces the number of steps needed to prepare polymer-grafted ceramic NPs; however, the method was not sufficient for mass production of polymer-grafted ceramic NPs. For industrial

applications of high-performance polymer-grafted NPs, mass production without sacrificing their performances must be achieved.

In order to solve this problem, a new method of preparing polymer-coated ceramic NPs has been developed. The method proposed here needs no reagent to connect inorganic surfaces and polymers, reduces the number of chemical processes, and enables densely polymer-coated ceramic NPs to be produced on a very large scale (more than 10 g of ceramic NPs can be coated at once in a 300-mL flask; see Figure S1 in the Supporting Information).<sup>8</sup> The polymer-coated NPs produced have similar structures to polymer-grafted NPs and block-copolymer-micelle-protected NPs, so their properties and performances are similar.<sup>9</sup>

The method is facile, as shown in Scheme 1. As a representative example, coating of several ceramic NPs (silica,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, BaTiO<sub>3</sub>, and TiN) by poly(2-hydroxyethyl acrylate)-b-polystyrene (PHEA-b-PS) was performed as follows: Ceramic NPs (1 g) were weighed, loaded in a 20-mL test tube with a screw cap, and transferred to an oxygen- and moisture-free glove box. Then, 2 mL of hydrophobic solvent (1:5 mixture of CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>) was added. The amount of solvent depends on the volume of the NPs; in the case of NPs with small BET surface areas, e.g., less than 50  $m^2\,g^{-1},$  2 mL or less of solvent is enough to immerse the particles, but in the case of very fine NPs with large BET surface areas, 5 mL of solvent is necessary to completely immerse the NPs. Dispersion of the ceramic NPs was enhanced by using an ultrasonicator (if necessary and/or possible, a homogenizer would be more effective). A hydrophilic monomer, i.e., 2-hydroxyethyl acrylate (HEA; 0.1g), 1 mg of a catalyst for reversible addition-fragmentation chain-transfer (RAFT) polymerization (benzyl hexyl trithiocarbonate), and 0.25 mg of a radical initiator [2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), V-70] were added to the test tube. Then, the test tube was sealed and the first polymerization was carried out, with vortex stirring, at room



Scheme 1. Illustration of encapsulation of ceramics nanoparticles by sequential living radical polymerization with particles (SqLRPwP).

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temperature. After 14 h for the first polymerization, 0.4 g of a hydrophobic monomer (styrene) was added to the test tube, and the second polymerization was carried out. After another 22 h, the test tube was removed from the glove box, and CHCl<sub>3</sub> was added to terminate the polymerization.

The as-synthesized NPs were washed three times with dimethyl sulfoxide (DMSO) by a dispersion and centrifugation method to remove residual monomers and free (unbound) polymers. In this case, no polymeric fraction was found in the supernatant, i.e., all the polymers synthesized were in the precipitate. After the purification processes, the polymer-coated ceramic NPs were dried overnight at 70 °C. The characterization of the polymer-coated NPs was carried out by field-emission scanning electron microscopy (FESEM), scanning transmission electron microscopy (STEM), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and dynamic light scattering (DLS). The molecular-weight distribution (MWD) of the polymer was measured using gel permeation chromatog-raphy (GPC) and NMR spectroscopy.

Figure 1 depicts the DLS results for PHEA-*b*-PS-coated BaTiO<sub>3</sub> NPs (BaTiO<sub>3</sub>@PHEA-*b*-PS). The *z*-average and peak size of the BaTiO<sub>3</sub>@PHEA-*b*-PS were almost the same size as those of BaTiO<sub>3</sub> NPs observed by SEM (Figure 2a). This implies that the BaTiO<sub>3</sub> NPs were coated separately by the polymers during the



**Figure 1.** DLS results of untreated BaTiO<sub>3</sub> NPs and BaTiO<sub>3</sub>@PHEA-*b*-PS in chloroform. The concentration of BaTiO<sub>3</sub> fraction was 0.01 wt % for both solutions. Inset depicts the image of BaTiO<sub>3</sub>@PHEA-*b*-PS in chloroform and dried BaTiO<sub>3</sub>@PHEA-*b*-PS. Very high concentration showed precipitation (a), on the other hand, when the concentration was lowered to 0.05 wt %, the dispersion was enough stable to measure DLS (b). The dried BaTiO<sub>3</sub>@PHEA-*b*-PS sheet (c).

polymerization. In the case of other smaller NPs like silica,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, TiN, and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, the NPs were not coated in a totally separated state but a few particles aggregated and agglomerated state. The initial particle size of BaTiO<sub>3</sub> was larger than those of the other NPs; therefore, the dispersion by ultrasonication was effective, although it was not strong enough for the other NPs, with initial particle diameters smaller than 100 nm. In addition, the BaTiO<sub>3</sub>@PHEA-b-PS could be separated by just evaporating the solvent, and they formed a BaTiO<sub>3</sub> solid sheet, shown in the inset image in Figure 1, not a powder. The BaTiO<sub>3</sub>@PHEA-b-PS solid was able to be repeatedly dispersed in CHCl<sub>3</sub>; however, the solid became elastic and difficult to redisperse after each solidification. The PS chains immobilized on the BaTiO<sub>3</sub> surface swelled in CHCl<sub>3</sub> and interpenetrated each other; therefore, redispersion became difficult. These results show that the PHEA-b-PS chains were strongly bound to the surface of the ceramic (BaTiO<sub>3</sub>).

The ceramic surface before and after coating with PHEA-*b*-PS was observed by FESEM. As shown in Figures 2a–2d, the ceramic surfaces after polymer coating were much smoother than those of the untreated ceramics. The SEM observations also show that the ceramics were successfully coated by the polymer. In addition, as shown in Figures 2e–2h, STEM images of PHEA-*b*-PS-coated SiO<sub>2</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs were recorded. Comparing the SEM- and TEM-mode images, it can be seen that all the SiO<sub>2</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs are covered with low-electron-density materials, which implies the formation of polymer layers on their surfaces.

In order to further examine the surface nature of the NPs and interactions between the ceramic NPs and polymer chains, the FTIR spectra of polymer-coated NPs, polymer-grafted NPs, PS, and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs were analyzed. Figure 3a (red line) shows the FTIR spectrum of the PHEA-b-PS-coated y-Fe2O3 NPs ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@PHEA-*b*-PS). The bands observed in the 3000–2800 and 3100-3000 cm<sup>-1</sup> regions were attributed to the C-H stretching modes of alkyl and aromatic groups, respectively. The bands at 1600 and  $1500-1430 \,\mathrm{cm}^{-1}$  correspond to the C-C vibration frequency of the PS aromatic group. The band at 1700 cm<sup>-1</sup> corresponds to the C=O vibration frequency of the carboxy group of PHEA. All these bands were clearly observed in the spectrum of y-Fe<sub>2</sub>O<sub>3</sub>@PHEA-b-PS. In addition, the intensities of the bands attributed to PS were stronger than those for PS-grafted  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-g-PS) prepared using a previously developed method.<sup>2</sup> This implies that the amount of immobilized PS was larger than that of directly PS-grafted  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, even though the



**Figure 2.** FESEM images of BaTiO<sub>3</sub> (a), BaTiO<sub>3</sub>@PHEA-*b*-PS (b), TiN (c), and TiN@PHEA-*b*-PS (d); SEM-mode STEM image of SiO<sub>2</sub> (e), TEM-mode STEM image of SiO<sub>2</sub>@PHEA-*b*-PS (f), SEM-mode STEM image of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (g), and TEM-mode STEM image of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@PHEA-*b*-PS (h).

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**Figure 3.** (a) FTIR spectra of PS (blue),  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@PHEA-*b*-PS (red),  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-*g*-PS (green), and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (black). (b) TG curves of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-*g*-PS (black). TG curves of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@PHEA-*b*-PS synthesized without any dispersing operation (blue), as-synthesized with ultrasonication and vortex mixing (green), and cleaned (red). Weight loss attributed to PHEA-*b*-PS was calculated from 300 °C.

background slope caused by scattering was smaller. This implies that the volume fraction of NPs loaded in the sample for FTIR of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@PHEA-*b*-PS was smaller than that of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-*g*-PS. The FTIR analysis also confirms that PHEA-*b*-PS was successfully immobilized on the surfaces of the ceramic NPs.

The amount of block copolymer immobilized was quantified by TG analysis. Figure 3b shows TG curves of directly PS-grafted and PHEA-*b*-PS-coated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> NPs. The amount of immobilized PHEA-b-PS was much higher than that of PS grafted by a direct grafting technique.<sup>2</sup> The amount of immobilized polymer was dependent on the dispersion method during the first polymerization step. When ultrasonication was used before polymerization, a very large amount of polymer was immobilized on the surface (red and green lines in Figure 3b). However, when no special dispersion method was used before and during the polymerization (with only stirring), a smaller amount of polymer was immobilized (blue line). Because dispersed particles have larger surface areas than aggregated particles, the dispersion operation is important for obtaining well-polymer-coated ceramic particles. The MWDs of polymers grown on the ceramic surfaces were also measured. Details are presented in the Supporting Information.<sup>8</sup> The polymer synthesized was actually a block copolymer of PHEA and PS, and the MWD of the PHEA-*b*-PS was  $M_{\rm n} = 47000$  Da, with  $M_{\rm w}/M_{\rm n} =$ 1.7.

The reason why the developed sequential reversible additionfragmentation chain-transfer polymerization with particles (SqRAFTwP) works well is now discussed. When a liquid with a large surface free energy (surface tension) is penetrated in a liquid (or gas) with a smaller surface free energy, the penetrated liquid forms spheres, such as water in air or organic solvents does. This phenomenon is thermodynamically spontaneous. SqRAFTwP is based on this simple principle. In addition, polymers with large surface free energies can be dissolved in hydrophobic organic solvents in their monomeric form. As the polymerization proceeds, the growing polymers (macroradicals) are precipitated in the solution. The place at which precipitation preferentially occurs is the ceramic surface. Covering the ceramic surface with the polymer is again thermodynamically preferable. According to the precipitation polymerization technique, the precipitated macroradical can still propagate;<sup>10</sup> therefore, follow-up propagations with monomers are possible. Polymers synthesized by follow-up polymerizations form the outer layer; again, this is thermodynamically stable. Because of the thermodynamically consistent procedure and the particle structure, block-copolymer-coated ceramic particles produced by SqRAFTwP are extraordinarily stable against solvents and heat. Ichinose and Kunitake reported that thin polymer films prepared by polymerization-induced adsorption had stronger interactions with ceramic surfaces than did those produced by simple coating,<sup>11</sup> this is another reason why the block-copolymer-coated NPs prepared by SqRAFTwP had stable polymer layers on their surfaces.

SqRAFTwP is also advantageous in terms of the principle of radical polymerization. The propagation rate coefficients of hydrophilic monomers in hydrophobic solvents are often larger than those in hydrophilic solvents.<sup>12,13</sup> This makes SqRAFTwP more attractive and powerful because the amount of hydrophilic monomers can be reduced to a negligible level, i.e., the adsorbing layer will not be so thick.

In conclusion, a new, facile, and effective procedure for preparing block-copolymer-protected ceramic NPs was developed. As described in the main text, operation of SqRAFTwP is very simple, but its theoretical background is strong; therefore, it is applicable to almost all ceramics. The method is also suitable for mass production of polymer-coated NPs. The developed method is expected to become one of the standard methods for producing polymer-coated NPs.

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