New micrometer-sized hemispherical magnetic/non-magnetic monodispersed polystyrene/poly(methyl methacrylate) composite particles: synthesis and characterization

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Composite micron and sub-micron-sized polymer particles with different morphologies are usually prepared by seeded dispersion or emulsion polymerization under different conditions, where a secondary monomer is polymerized in the presence of seed latex particles, with or without the pre-swelling of the seed particles by the second monomer. By controlling the polymerization process variables, seeded dispersion or emulsion polymerization can produce structured latexes exhibiting a wide variety of particle morphologies such as core-shell, hemispherical, or inverted core-shell particles in which second-stage polymer is incorporated at the center of the particle, and the seed polymer is located on the periphery of the composite particle. The mechanism of producing various morphologies is based on the heterogeneous structures generated by the phase separation of the different polymers in the particles during polymerization, and is controlled by two major factors concomitantly acting in the system [1–5]: thermodynamic factors that determine the equilibrium morphology of the final composite latex particles, and kinetic factors that determine the ease with which the thermodynamically favored equilibrium morphology can be achieved [6]. Most of the studies on non-spherical composite microparticles based on the phase separation of two immiscible polymers have been performed with polymers which do not contain functional groups (e.g. Polystyrene/Poly(n-butyl methacrylate)) through which covalent binding of appropriate ligands, or other desired properties, may be achieved.

Recently, Du *et al.* [6] prepared hemispherical poly(2-hydroxylethyl methacrylate-co-methyl methacrylate)/poly(styrene-co-glycidyl methacrylate) sub-micron composite polymer particles bearing hydroxyl and oxirane groups on either side. These composite particles were prepared by soap-free seeded emulsion polymerization using P(HEMA-MMA) seed particles cross-linked by ethylene glycol dimethacrylate and 2,2′-azobis(2-amidinopropane).2HCl (V-50) as an initiator. The objective of these studies was to synthesize hemispherical nanospheres with different functional groups on either side, which can be stage-modified by chemical and biological molecules to conjugate with chemical and biological nanosystems.

Recently, we submitted for publication studies describing the use of a single-step swelling method for the synthesis of hemispherical bi-functional micron-scaled polystyrene/poly(n-butyl methacrylate) (PS/PBMA) composite particles with controllable bulk and surface composition. We have demonstrated that selective functionalization of the PBMA surface of the PS/PBMA composite particles can be achieved by direct surface reaction of hydrophilic vinylic monomers such as acrylamide dissolved in the water media with BMA oligoradicals polymerizing within uniform PS template microspheres, resulting in polyacrylamide grafted specifically on the PBMA surface of the PS/PBMA composite particles.

In the present studies, magnetic uniform PS microspheres were prepared by coating monodispersed PS microspheres of 2.4 ± 0.2 μm diameter, prepared by dispersion polymerization of styrene in ethanol in the presence of the stabilizer polyvinylpyrrolidone [7, 8], with successive thin layers of crystallized Fe_3O_4 according to a procedure similar to that described in [9]. Briefly, an aqueous suspension containing 350 mg of the PS microspheres in 350×10^{-6} m^3 of distilled water was sonicated at room temperature for a few minutes. The suspension was mechanically stirred, while the temperature was preset to 60 °C. Nitrogen was bubbled through the microspheres' suspension during the coating process to exclude air. Volumes of 0.5×10^{-6} m^3 of reference aqueous solutions of $FeCl_2\cdot4H_2O$ (25 mM) and 0.5×10^{-6} m^3 of $NaNO_2$ (1.5 mM) were successively introduced into the reaction flask. Thereafter, an aqueous solution of sodium hydroxide (50 mM) was added until a pH of about 9.5 was reached. This procedure was repeated 18 times. During this coating process, the PS microspheres became brown-black in color. The suspension was then cooled to room temperature. The magnetic PS microspheres were washed extensively in water and then dried by lyophilization. Figs 1A and B illustrate scanning electron microscope (SEM) micrographs of non-magnetic and magnetic PS microspheres, respectively. Fig. 1B reveals discontinuous islands of Fe_3O_4 of 30–40 nm thick, coating the polystyrene microspheres. Thermogravimetric and elemental analyses showed that the magnetite content of the magnetic PS microspheres is approximately 10% (w/w). The magnetization of the magnetic microspheres as a function of external field strength, measured by a vibrating sample magnetometer (VSM), is

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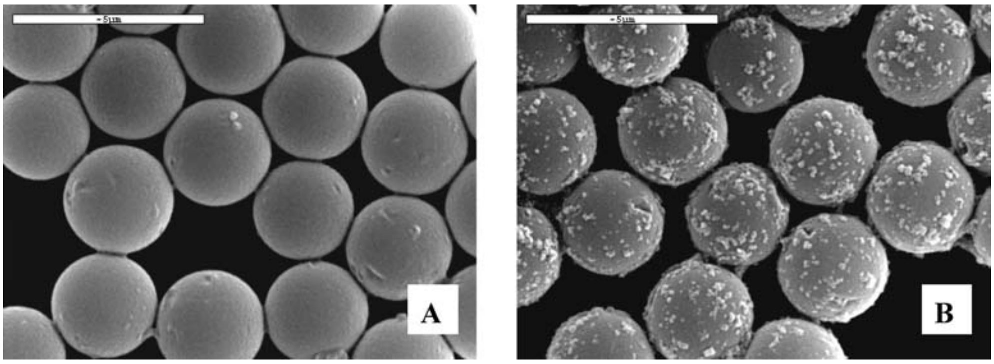

Figure 1. SEM micrographs of the PS microspheres (2.4 μm average diameter) before (A) and after (B) coating with Fe_3O_4.

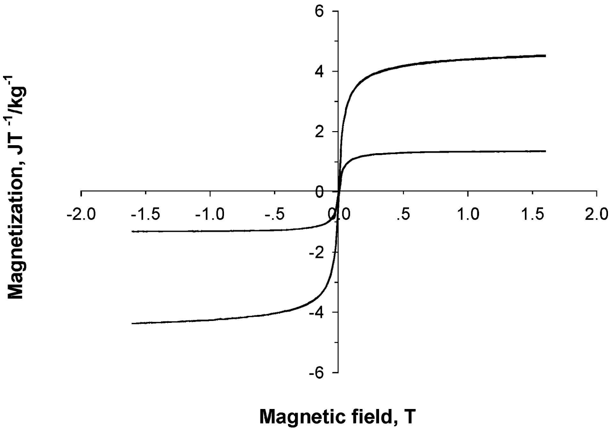

Figure 2. Magnetization curves for magnetic PS microspheres (A) and magnetic/non-magnetic PS/PMMA composite particles (B).

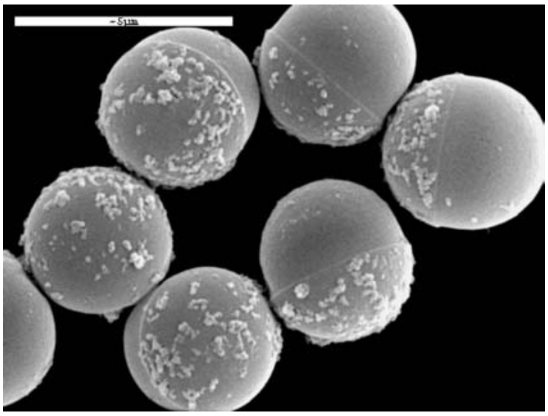

Figure 3. SEM micrographs of magnetic/non-magnetic PS/PMMA composite particle.

illustrated in Fig. 2A. The saturation magnetization reached at ca. 0.5 T was 4.2 JT^{-1} kg^{-1}.

The magnetic PS microspheres were then used as template for the preparation of hemispherical magnetic/non-magnetic polystyrene/poly (methyl methacrylate) (PS/PMMA) composite particles. For this purpose, the magnetic PS template microspheres were swollen by a single step swelling process [10] with methyl methacrylate (MMA) containing the initiator benzoyl peroxide (BP) followed by polymerization at 73 °C. Briefly, the dried magnetic PS template microspheres were first dispersed in 30×10^{-6} m^3 aqueous solution containing 1.5% (w/v) of the surfactant sodium dodecyl sulfate (SDS). In a separate vial, 16.5 $\times$ 10^{-6} m^3 of 1.5% (w/v) SDS aqueous solution were added to 0.6 $\times$ 10^{-6} m^3 MMA containing 6 mg (1% w/v) BP. MMA emulsion (droplets size < 0.4 μm) was then formed by sonication of the former mixture at room temperature for 1 min. Thereafter, 3.5 $\times$ 10^{-6} m^3 of the suspension of the magnetic PS template microspheres were added to the stirred MMA emulsion. Kinetics studies of the swelling of the magnetic PS template microspheres by MMA indicated that under the experimental conditions the swelling rate was very fast, and completed within ca. 5 min. The completion of the swelling process was verified by the disappearance of the small droplets of the emulsified MMA from the swollen particles dispersion as observed by light microscopy. Before polymerization, sodium nitrite (0.1% w/v) was dissolved in the water media in order to prevent polymerization of MMA in the aqueous media. For polymerization of MMA in the swollen particles, the vial containing these particles was shaken at 73 °C for 20 h. Excess MMA was then evaporated for 48 h at room temperature, and the particles were then washed by extensive centrifugation cycles with water and then air dried.

Fig. 3 illustrates SEM micrographs of typical samples of the formed PS/PMMA composite particles. The 3.8 μm diameter composite particles clearly appear to have hemispherical morphology with two distinct phases: magnetic PS and non-magnetic PMMA. Thermogravimetric and Elemental analyses illustrate that the formed particles are composed of 51.6% PMMA, 45.0% PS and 3.4% iron oxide coating (w/w). The magnetization of the PS/PMMA composite particles as a function of external field strength, measured by VSM, is illustrated in Fig. 2B. The saturation magnetization reached at ca. 0.5 T was 1.4 $JT^{-1}kg^{-1}$, i.e. ca. 1/3 the magnetization of the template magnetic PS microspheres (Fig. 2A), as expected from the reduction of the percent magnetic coating of the PS/PMMA composite relative to the magnetic PS template particles.

The potential use of spherical and non-spherical magnetic polymeric microparticles for biomedical applications (e.g. specific cell labeling and separation) as well as others, e.g. optical uses (photonic bandgap crystals, magnetically modulated optical nanoprobes, etc.) has been shown in [11–13]. We have demonstrated an effective route to microscale non-spherical magnetic/non-magnetic composite particles of hemispherical morphology. We plan in the future to extend this approach also to PS template nanoparticles (diameter <100 nm). The ability to change the% ratio of the magnetic/non-magnetic parts as well as the bulk and surface compositions in these particles, via controlling the percent of iron oxide coating, the% ratio PS/PMMA and the other polymerization parameters (e.g. initiator concentration) will provide additional ways to control the properties of these particles. Currently, more detailed studies of the synthesis, characterization and the use of these monodispersed composite particles are underway in our laboratory.

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