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# Surface-modified hemispherical polystyrene/polybutyl methacrylate composite particles

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## Abstract

Micrometer-sized polystyrene/poly(*n*-butyl methacrylate) composite particles of hemisphere morphology and narrow size distribution were prepared by a process of single-step swelling of uniform polystyrene template microspheres with emulsion droplets of the monomer *n*-butyl methacrylate containing the initiator benzoyl peroxide in the presence, or absence, of the co-swelling agent toluene. Butyl methacrylate was then polymerized at 73 °C within the template microspheres. Surface and bulk characterization of the particles were performed by methods such as FTIR, elemental analysis, XPS, advancing contact angle, light microscope, SEM, and cross-sectional TEM. Selective surface functionalization of the poly(*n*-butyl methacrylate) phase of the composite particles was performed by carrying out a similar swelling and polymerization process in the presence of a water-soluble vinylic monomer such as acrylamide.

*Keywords:* Microspheres; Poly(*n*-butyl methacrylate); Template; Composite; Hemisphere; Single-step swelling

## 1. Introduction

Composite micrometer- and sub-micrometer-sized polymer particles with different morphologies are usually prepared by seeded dispersion or emulsion polymerization (respectively) under different conditions, where a secondary monomer is polymerized in the presence of seed latex particles, with or without the preswelling of the seed particles by the second monomer. By controlling the polymerization process variables, seeded dispersion or emulsion polymerization can produce structured latices 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 morphology of two-stage latex particles 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. Seeded polymerization for the dispersion of highly monomer-swollen polymer particles gives composite polymer particles having a comparatively thermodynamically stable morphology [6]. On the other hand, seeded dispersion polymerization, in which almost all monomers and initiators exist in the medium, may result in kinetically controlled core–shell morphology in which layers of the second polymer accumulate in their order of formation, even if the morphology is unstable thermodynamically [7]. Some composite polymer particles produced by seeded emulsion polymerization, which consist of two kinds of homopolymers, have confetti-like, raspberry-like [3] and void [8] morphologies. 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.

Most of the studies on nonspherical composite microparticles based on the phase separation of two immiscible

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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. [9] prepared hemispherical poly(2-hydroxylethyl methacrylate-co-methyl methacrylate)/poly(styrene-co-glycidyl methacrylate) submicrometer composite polymer particles bearing hydroxyl and oxirane groups on either side by soap-free seeded emulsion polymerization using P(HEMA-MMA) seed particles crosslinked by ethylene glycol dimethacrylate using $2,2'$-azobis(2-amidinopropane) · 2HCl (V-50) as an initiator. The objective of their work was to synthesize hemispherical nanospheres containing different functional groups on either side, which can be stage-modified by chemical and biological molecules to conjugate with chemical and biological nanosystems. Furthermore, Du et al. have succeeded [10] in the development of a new heterobifunctional poly(glycidyl methacrylate-co-divinylbenzene)/polystyrene latex beed bearing an enzyme on one side and biotin on the other.

A new method for preparing micrometer-sized particles of narrow size distribution and controlled properties, i.e., surface area, based on a single-step swelling process of uniform PS template microspheres was recently published by Margel and co-workers [11,12]. According to this process, the swelling of the template particles with the initiator and monomer/s via a swelling solvent is accomplished in a single step, in contrast to the multistep swelling process, where the swelling with these reagents is accomplished in two or more steps [13–20]. Furthermore, in the multistep swelling process, as well as in the dynamic swelling method (DSM) [21,22], the template particles occupy a small portion of the final polymerized particle (typically less than 1%). On the other hand, in the single-step swelling method developed in our laboratory, the template particles may occupy a high portion of the formed composite particles, about 25%. Further differences between the single-step swelling method and the multistep or DSM processes are discussed in Refs. [11,12].

Previous studies carried out in our laboratory concerning the single-step swelling process of PS particles were accomplished with monomers that produced polymers miscible with the PS template matrix (e.g., styrene, divinylstyrene, and chloromethylstyrene) and thus did not phase separate [11]. In contrast, the present studies describe the behavior of a single-step process of PS template microsphere swelling with monomers (e.g., BMA) that produce polymers (e.g., PBMA) immiscible with the template PS.

The present paper describes the synthesis and characterization of micrometer-sized polystyrene/poly(*n*-butyl methacrylate) (PS/PBMA) composite particles of hemispherical morphology and narrow size distribution by a process of single-step swelling of uniform PS template microspheres with emulsion droplets of BMA containing BP, followed by polymerization of BMA at 73 °C within the template microspheres. The effect of a co-swelling agent such as toluene is discussed. A similar polymerization process in the presence of an aqueous solution containing a functional hydrophilic vinylic monomer, e.g., acrylamide, resulted in similar particles containing surface amide groups located on the surface of the PBMA phase of the composite particles. These uniform functional hemispherical composite particles with controllable bulk and surface composition synthesized by the method suggested herein may be used in various fundamental and practical applications, e.g., plastics engineering, three-dimensional structures, and self-assembly processes.

## 2. Materials and methods

### 2.1. Chemicals

The following analytical-grade chemicals were purchased from Aldrich and were used without further purification: BP (98%), sodium dodecyl sulfate (SDS), polyvinylpyrrolidone (PVP) with molecular weight 360,000, 2-methoxyethanol (HPLC), ethanol (HPLC), toluene, BMA, and acrylamide. Styrene (Aldrich 99%) was passed through activated alumina (ICN) to remove inhibitor before use. Water was purified by passing deionized water through an Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, UK).

### 2.2. Synthesis of PS template microspheres

Uniform PS template microspheres were prepared according to a procedure similar to that described in the literature [23–25]. Briefly, these microspheres were synthesized in a three-neck round-bottom flask equipped with a condenser and immersed in a constant-temperature silicone oil bath at a preset temperature. In a typical experiment, PS microspheres with average diameter $2.3 \pm 0.2$ µm were formed by introducing into the reaction flask (1 l) a solution containing PVP, MW 360,000 (3.75 g, 1.5% w/v of total solution), dissolved in a mixture of ethanol (150 ml) and 2-methoxyethanol (62.5 ml). The temperature of the mechanically stirred solution (200 rpm) was then preset to 73 °C. Nitrogen was bubbled through the solution for ca. 15 min to exclude air, and then a blanket of nitrogen was maintained over the solution during the polymerization period. A deaerated solution containing the initiator BP (1.5 g, 0.6% w/v of total solution) and styrene (37.5 ml, 16% w/v of total solution) was then added to the reaction flask. The polymerization reaction continued for 24 h and was then stopped by cooling. The formed microspheres were washed by extensive centrifugation cycles with ethanol and then with water. The particles were then dried by lyophilization.