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Fabrication of shape-tunable macroparticles by seeded polymerization of styrene using non-cross-linked starch-based seed

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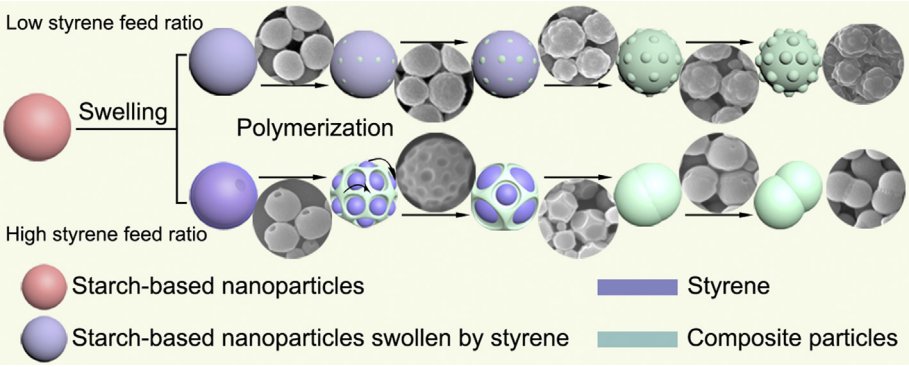
GRAPHICAL ABSTRACT



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ABSTRACT

Nonspherical colloidal particles with various geometries and different compositions have attracted tremendous attention and been widely researched. The preparation of polymer colloidal particles with controlled shapes by seeded polymerization is recognized as the most promising technique owing to the precise control of various morphologies and using non-cross-linked seed particles are of particular interest. Seeds particles derived from natural biopolymers are seldom applied. Hence, non-cross-linked starch-based seed could be used to fabricate the anisotropic particles by soap-free seed polymerization.

Non-cross-linked starch-based seed particles were prepared by a nanoprecipitation method. Starch/polystyrene composite colloidal particles with shape-tunable were fabricated by soap-free seeded polymerization using starch-based seed. The effect of the polymerization time, monomer feed ratio and seed type were investigated.

The seed particles with a single- or multi-hole structure were obtained after swelling with styrene. The resulting particles including golf-like, raspberry-like, octahedron-like and snowman-like structures, was fabricated on the polymerization process. This study firstly reports that the morphology of composite particles from golf-like to snowman-like at high monomer feed ratio using starch-based seed. At low

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monomer feed ratio, raspberry-like particles were obtained by surface nucleation increasing process. In addition, seed type also effect the morphology of composite particles.

1. Introduction

Nonspherical colloidal particles with various geometries and different compositions have attracted tremendous attention and been widely researched because of their potential application as solid surfactants [1–4], drug delivery systems [5,6], coatings [7], and functionalizing particles [8].

Up to now, various methods for the preparation of polymer particles with controlled shapes have been proposed, including phase separation [3,9–11], microfluidics [12,13], and selective surface modification [14,15]. Among these methods, seeded polymerization is recognized as the most promising technique owing to the precise control of various morphologies, such as raspberry-like [16], snowman-like structures [4,17], and other nonspherical composite particles [18]. This method involves two steps: firstly, the cross-linked seed particles are prepared by heterophase polymerization (dispersion polymerization, emulsion polymerization and suspension polymerization) using a variety of monomers and swelling of cross-linked seed particles with the monomer and/or solvents; secondly, polymerization of the monomers in liquid protrusions leads to the formation of nonspherical particles by forcing phase separation after polymerization [1–3,8]. To our knowledge, polymeric particles such as polystyrene (PS) [1,3,10,19,20], poly(methyl methacrylate) (PMMA) [17], poly(vinylidene fluoride) (PVDF) [21,22], and poly(glycidyl methacrylate) (PGMA) [18,23] have been widely used as seed particles in seed polymerization to fabricate particles with controllable morphologies. Generally, a surfactant is necessary to avoid aggregation during the polymerization process. Furthermore, the seed particles should be previously cross-linked to maintain their shape and facilitate the formation of nonspherical particles by forcing phase separation after polymerization.

On the other hand, the degree of cross-linked of seed particles is one of the important factors determining the swelling capacity during the monomer swelling of seed particles, and the degree of phase separation in the polymerization process [24]. The anisotropic particles fabricated by soap-free polymerization using non-cross-linked seed particles are of particular interest. Yu et al. [25] have fabricated anisotropic poly(vinyl chloride-co-acetoacetoxyethyl methacrylate)/polystyrene (P(VC-co-AAEM)/PS) nanoparticles with controllable morphologies using non-cross-linked P(VC-co-AAEM) particles as seed particles via emulsifier-free seeded emulsion polymerization. Pan et al. [26] have prepared anisotropic poly(tert-butyl acrylate)/polystyrene (PtBA/PS) composite particles with controllable morphologies using non-cross-linked PtBA seed particles by soap-free seeded emulsion polymerization. Zhang et al. [18,23] have fabricated poly(glycidyl methacrylate)/polystyrene (PGMA/PS) patchy microparticles with controllable morphologies using non-cross-linked single-hole PGMA seed microparticles by seed emulsion polymerization. It is noted that all the above-mentioned seed particles were fabricated by a heterophase polymerization process. As a result, it is necessary to widen the range of seed types and discover simple and feasible production methods for these seeds. In addition, seed particles derived from natural biopolymers are seldom applied.

We have shown recently that raspberry-like starch/PS particles can be prepared by Pickering polymerization of styrene, initiated by a water-solution initiator using starch-based nanoparticles (SNPs) as particulate emulsifiers [27], while monodisperse core-shell particles can be fabricated by seeded polymerization of styrene initiated by an oil-solution initiator using starch-based nanoparticles (SNPs) as seed particles [28]. In this paper, starch/PS composites with tunable micromorphology were synthesized through soap-free seed polymerization using non-cross-linked SNPs as a seed. This strategy includes: (1) the preparation of SNP seed through a self-assembly approach; (2) seed polymerization of styrene using SNPs as a seed in the absence of surfactant; and, (3) fabricating starch/PS composite particles with tunable shape, including golf-like, raspberry-like, octahedron-like and snowman-like structures. In this process, SNPs simultaneously serve as a seed and stabilizer, and undergo swelling, nucleation, and morphological transition during the polymerization process. Moreover, the geometrical morphology of the resultant particles can be regulated by adjusting the polymerization time, monomer feed ratio and seed type. On the basis of the experimental results, we propose a formation mechanism for the geometrical composite particles.

2. Experimental

2.1. Materials

Styrene (Sigma-Aldrich) was distilled under reduced pressure to remove inhibitor and stored in a refrigerator (4 °C) until use. Octenyl succinic anhydride (OSA) (Sigma-Aldrich), acetic anhydride (AC) (Sigma-Aldrich), 4-dimethylaminopyridine (DMAP) (Sigma-Aldrich), and ammonium persulfate (APS) (Sigma-Aldrich) were used directly without further purification. Starch-mixed ester (S-AC-OSA) was synthesized by a previous method [27,28]. Deionized water was used in all the experiments.

2.2. Fabrication of the starch-based seed particles (SNPs)

Non-cross-linked SNP seed particles were fabricated by a nanoprecipitation method. Firstly, different types of S-AC-OSA were synthesized by a previous method [27,28], presented in the Supporting Information. The degree of substitution by acetylation and octenyl succinic esterification determined by ^{1}H NMR is presented in Table 1 and Fig. S1 in the Supporting Information. SNP seed particles were prepared by dropwise addition of the aqueous solution to the S-AC-OSA polymer acetone solution. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterization indicates that spherical nanoparticles are obtained after the acetone has completely evaporated (Fig. 1). Dynamic light scattering (DLS) measurements indicates that the size and size distribution of the SNPs are 400 nm and 0.375, respectively (Fig. 1C). In order to explore the effect of seed particles type on the formation of composite particles, different degree of substitution of the OSA group (DS_{OSA}) of the seed particles were prepared by a nanoprecipitation method using starch-mixed esters with different DS_{OSA} shown in Fig. S2.

2.3. Preparation of composite particles

The recipes are summarized in Table 1. A typical procedure was as follows. Briefly, 1.8 g of styrene and 50 g of a SNP suspension (containing 0.15 g of SNPs) were added to a 100 mL three-neck round-bottom flask equipped with a reflux condenser and a nitrogen inlet in an oil bath. The mixture was stirred at a speed of 200 rpm using a mechanical stirrer and purged with nitrogen. After the