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Hybrid latex particles preparation with seeded semibatch emulsion polymerization

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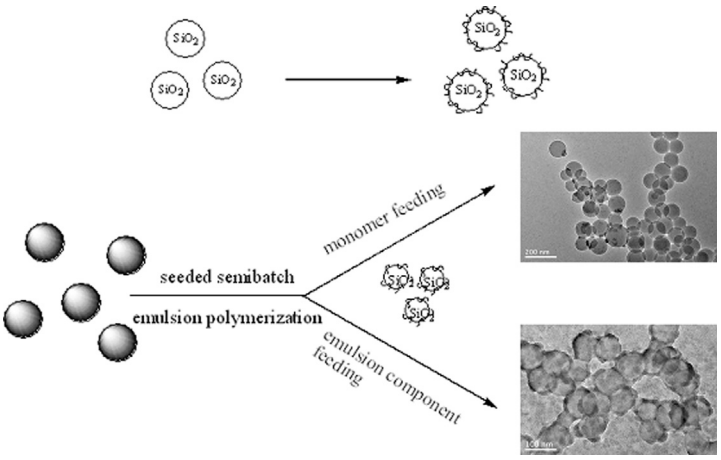
HIGHLIGHTS

- The raw silica is modified by block copolymer.
- The styrene mixed with modified silica is used in polymerization.
- Hybrid latex is prepared by seeded semibatch emulsion polymerization.
- The modified silica was well-distributed on the seeded latex surface.
- The prepared film surface showed more bright spots and convex structures.

GRAPHICAL ABSTRACT



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ABSTRACT

Hybrid latex particles of modified nano silica and polystyrene were prepared by seeded semibatch emulsion polymerization. The block copolymer of styrene (St) and vinyltrimethoxysilane was synthesized by reversible addition-fragmentation chain transfer polymerization using as a modifying agent for improving the silica dispersion property in St. In seeded semibatch emulsion polymerization, hybrid latex particles were prepared by feeding a monomer mixture or emulsion component that contained modified silica. The effects of the feeding material, feeding rate and SLS concentration of the emulsion components on the St conversion (instantaneous conversion and cumulative conversion), the resultant latex particles size, distribution and morphology were discussed. With the St monomer mixture at a 5.0 g/h feeding rate, the instantaneous conversion was approximately 75%, and the resultant latex particles Z average diameter and particle size distribution was 99.5 nm and 0.06, respectively. The modified silica was uniformly distributed at the seed latex surface. The prepared film surface exhibited more bright spots, and convex structures were observed by atomic force microscopy. The Si atom content was 2.5%, as measured by X-ray photoelectron spectroscopy.

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1. Introduction

In recent years, organic/inorganic hybrid particles have increasingly attracted the attention of researchers because of their outstanding characteristics [1–4]. Several polymerization techniques for organic/inorganic hybrid particles have been developed, such as the sol-gel method [5–7], in-suit polymerization [3,8–9], and the blending method [10–12]. Among the diverse polymerization methods for preparing composite particles, the heterophase polymerization processes, including conventional emulsion polymerization [13–15], miniemulsion polymerization [16–19] and microemulsion polymerization [20–21], are environmentally friendly alternatives to solvent-based systems.

Some groups have obtained organic/inorganic hybrid particles via heterophase polymerization. Ni [15] and his partners prepared SiO_2/PS (polystyrene) composite particles via conventional emulsion polymerization and studied the effect of the amount of the silane coupling agent on the polymerization. SiO_2/polyacrylate latex particles with high thermal stability were prepared by using triethoxyvinylsilane as a "bridge" between silica and polyacrylate. Zhang et al. [19] prepared ZnO/PS core-shell hybrid microspheres by miniemulsion polymerization using 3-(trimethoxysilyl)-propyl methacrylate (MPS) as a functional comonomer.

Herein, SiO_2/PS nano hybrid particles were prepared via seeded semibatch emulsion polymerization. The silica was modified by the block polymer firstly, which was a copolymer of styrene (St) and vinyltrimethoxysilane (VTMS) synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT), to improve the dispersion property in St. Then, the monomer mixture (St and raw/modified silica) and emulsion component (St, modified silica, emulsifier and deionized water) were fed into the seeded emulsion system at a constant rate. The resultant latex particle diameter and particle size distribution (PSD) were measured. The morphology of the hybrid particles was observed. The effects of different seeded semibatch emulsion polymerization methods on the coated film surface properties were discussed.

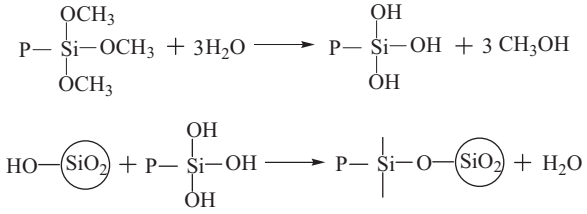

Fig. 2. Modification process of silica.

2. Experimental

2.1. Materials

Styrene (Shanghai Lingfeng Chemistry Reagent Co. Ltd.) was purified upon distillation under reduced pressure and was kept refrigerated until use. 2,2-Azobisisobutyronitrile (AIBN) of analytical purity was supplied by No.2 Shanghai Reagent Co., Ltd, China. VTMS of chemical purity was purchased from DeBang Chemical New Materials Co., Ltd. 2-cyanoprop-2-yl L-dithionaphthaLate (CPDN) was synthesized according to the literature [22]. Toluene, sodium lauryl sulfate (SLS) surfactant and potassium persulfate (KPS) (Shanghai Lingfeng Chemistry Reagent Co. Ltd.) were analytical grade and were used as received. The specification of raw silica (Cabot Co. Ltd., USA.) was M5; the primary particle diameter was 12 nm. Deionized water was used for all polymerization and treatment processes.

2.2. Block copolymer prepared as modifying agent

For the polymerization of the macromolecular chain transfer agent, 2.5 g St, 0.025 g CPDN, and 0.012 g AIBN were fully mixed and injected into a 10 mL ampere bottle. The bottle was placed under vacuum while cooling under liquid-nitrogen, refilled with nitrogen and finally sealed. The polymerization temperature was

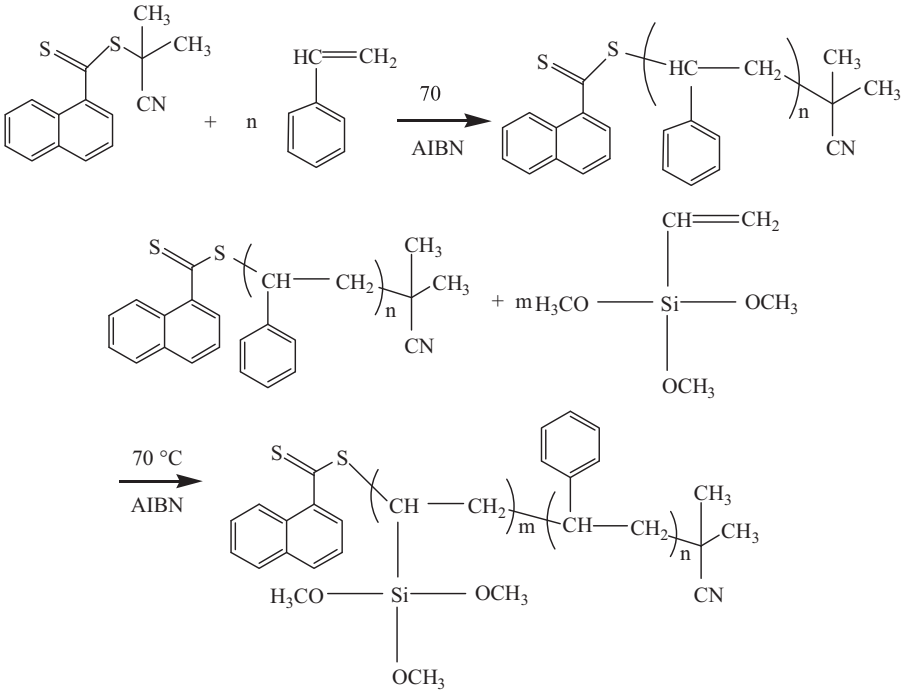

Fig. 1. General reaction routes for the synthesis of P (St-b-VTMS).