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Synthesis of poly(methyl methacrylate) nanoparticles via differential microemulsion polymerization

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ABSTRACT

Poly(methyl methacrylate) nanoparticles are synthesized via differential microemulsion polymerization, where the monomers in the reaction system are kept at very low concentrations by continuous differential addition. The effects of various reaction conditions, such as initiator, surfactants, reaction temperature and monomer loadings, on the particle size and molecular weight have been investigated. The effects of initiator and reaction temperature on latex particle numbers and polymer chain numbers within the particles were also investigated. It was observed that the dependence of particle size on reaction temperature and initiator concentration was non-monotonic. The optimized conditions were screened to prepare nanoparticles with the smallest size.

1. Introduction

Polymer nanomaterials have received much attention due to their special properties arising from their small size. Owing to the high surface/volume ratio of the small particles, the percentage of molecules or atoms on the surface is greatly increased. These properties are very desirable for applications in various fields, such as drug delivery [1–4], sensors [5,6], molecular gels [7,8], semiconductors [9], catalysts [10,11], environmental applications [12] and industrial applications [13]. A variety of methods have been reported to prepare polymer nanoparticles, such as solvent evaporation [14], molecular assembly [15], template chemistry [16], dendrimer polymerization [17], mechanical pulverization [18], microemulsion polymerization [19] and miniemulsion polymerization [20]. In these methods, microemulsion polymerization and miniemulsion polymerization are the most widely used methods. Microemulsion polymerization was first reported in the early 1980s [21]. This process can produce transparent or translucent polymer microlattices with particle diameters as small as 10 nm, while the particle diameters by conventional emulsion polymerization are generally 50–300 nm [22]. However, two major drawbacks have limited the applications of microemulsion polymerization: (1) high surfactant/monomer weight ratios, usually larger than 1, are required to produce small particles; (2) only a low solid content, usually less than 10 wt.%, could be made. Thus, expensive purification procedures would be required to remove surplus surfactant and to concentrate the lattices. Miniemulsion polymerization is a method that uses water-insoluble monomers or water-insoluble reagents to make fine particles, by which the obtained particle sizes are usually in the range of 50–500 nm [23], with a wider particle size distribution (PSD) than that obtained by microemulsion polymerization. In addition, for a miniemulsion polymerization system, a high shear force is usually required to produce small particles, which is usually not preferred in applications. Hence, it is imperative to find a more practical method for nanoparticles preparation. Gan et al. [24] reported

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the polymerization of methyl methacrylate in ternary Winsor I-like systems, in which cetyltrimethylammonium bromide (CTAB) was used as surfactant. Although relatively high polymer/surfactant weight ratios (around ~8:1) were achieved in their systems, the produced particle sizes were still quite large (30–60 nm), and the particle size distribution was rather broad. Ming et al. [25] reported a modified microemulsion polymerization process to prepare nanosize PMMA latex with a high solid content, in which the diameters were lower than 20 nm and relatively concentrated (10–30 wt.%) latexes were attained; however, the weight ratio of surfactant/polymer (1/10) was still relatively high. Chen and Zhang [26] used a γ-ray-induced method for the polymerization of methyl methacrylate in a microemulsion system, which is stabilized by a mixture of sodium 12-acryloxy-9-octadecenoic acid (AOA) and sodium dodecyl sulfate (SDS) at room temperature. The transparent microlattices produced had higher monomer contents (up to 38.6 wt.%); however they still required a relatively high amount of surfactant (5.5 wt.%), and the particle size of the lattices was larger than 30 nm. Chen et al. [27] reported a new monomer feeding system for microemulsion polymerization and PMMA nanoparticles were produced with a number-average diameter of 18.4 nm and the surfactant/monomer weight ratio was at about 0.15, which was high as well. To explore a practical technical route in which the surfactant amount required could be significantly decreased and the nanoparticle size could be controlled, a differential microemulsion polymerization was proposed [28], in which, the monomer was continuously added at such a low speed that the monomer content in the reaction system is at a differential level, but not a starved level. With this strategy, it was confirmed that the reaction conditions could be milder than those required in regular emulsion polymerization processes [28–32], and the particle size realized was similar to or even smaller than that produced by microemulsion polymerization.

Although a few papers [28–30,32] have reported the investigations on the synthesis of nanosized PMMA via differential microemulsion polymerization, the emphasis of the previous studies was mainly focused on the development of the methodology and the minimization of the surfactant amount needed. The objective of this study is to further simplify the recipes by eliminating the use of a co-surfactant and to investigate the effects of various operational parameters, such as initiators, surfactants, monomer amount, and reaction temperature, involved in the differential microemulsion polymerization, on the performance of the polymerization reaction, and to reveal the optimal conditions for synthesizing the smallest nanoparticles.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) (CP grade, Sinopharm Chemical Reagent Co., Ltd., China), sodium dodecyl sulfate (SDS) powder (purity ⩾ 86%, Sinopharm Chemical Reagent Co., Ltd., China), ammonium persulfate (APS) (AR grade, Sinopharm Chemical Reagent Co., Ltd., China), calcium chloride anhydrous (AR grade, ⩾96% purity, Sinopharm Chemical Reagent Co., Ltd., China), cetyltrimethylammonium bromide (CTAB) (AR grade, ⩾99% purity, Sinopharm Chemical Reagent Co., Ltd., China) and TritonX-100 (emulsifier OP) (CP grade, Sinopharm Chemical Reagent Co., Ltd., China) were used as received. Deionized water was used as obtained from the College of Chemistry, Chemical Engineering and Materials Science of Soochow University, Suzhou, China.

2.2. Preparation of PMMA nanoparticles

PMMA nanoparticles were prepared by differential microemulsion polymerization, which means only a differential amount of the monomer existed in the reaction system during the reaction period. The operational procedures for the reaction were similar to those presented elsewhere [28]. Simply, the initiator and surfactant were mixed in a certain amount of water in a 250 cm^3 four-necked Pyrex glass reactor (SAMDUK, China), equipped with a magnetic stirrer, a reflux condenser, a thermometer and a dropping funnel. When the temperature in the system reached a designated level, MMA was continuously added as small droplets (at a given rate of 0.15 ± 0.02 mL min^{-1} via a dropping funnel) for a specified period of time to achieve the differential level of the monomer content in the reaction system. After completion of the MMA addition, the reaction system was maintained at the reaction temperature for a certain aging time before cooling.

2.3. Separation of polymer samples for characterization

The resultant polymer was precipitated using a saturated calcium chloride solution and was separated by a vacuum filtration technique. The surfactant, calcium chloride and initiator were washed off the particles three times with a sufficient amount of warm de-ionized water.

2.4. Characterization of the synthesized products

The compositions of the resultant polymers were analyzed by Fourier transform infrared spectroscopy (Thermo Nicolet iS10, USA).

The *Z*-average particle size and the distribution of the particle size were measured by a laser particle size analyzer (Malvern Zetasizer Nano-ZS, UK).

The number-average-molecular weight (M_n) and weight-average molecular weight (M_w) as well as the molecular weight polydispersity index (PDI) were determined using a Waters 1515 gel permeation chromatograph (GPC, Waters, USA) equipped with a refractive index detector (Waters 2414), using HR1, HR2, and HR4 (7.8×300 mm^2, 5 mm beads size) columns which allows the measurement of molecular weights over the range of 10^2–5×10^5 g mol^{-1}. THF was used as the eluent at 30 °C with a flow rate of 1.0 mL min^{-1}. The GPC samples were injected using a Waters 717 plus autosampler and calibrated with PMMA standards from Waters.