Macromolecular Nanotechnology

Synthesis of styrene–butadiene copolymer nanoparticles via semi-batch differential microemulsion polymerization

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ABSTRACT

Styrene–butadiene rubber (SBR) nanoparticles were prepared in a semi-batch differential microemulsion polymerization (DMP) system using sodium oleate as the emulsifier. The size of the SBR nanoparticles could be easily tailored by controlling the monomer addition speed, the reaction temperature, the composition of the monomer feed stream and the amount of a surfactant introduced to the process. The smallest particle size, which is about 8 nm, was achieved at 70 °C with a very low surfactant concentration (25 mM) as well as a reasonable conversion (72%). Moreover, the effects of n-dodecyl mercaptan (n-DDM), which was used as the chain transfer agent, on the particle size and the reaction conversion were investigated. Larger spherical particles and higher reaction conversions were observed at a higher n-DDM concentration. n-DDM can well regulate the SBR molecular weight of a polymer and a higher n-DDM concentration resulted in a smaller molecular weight. The DMP is found to be a very effective approach that requires a minimum amount of surfactant to prepare fine-tuned polymeric nanoparticles.

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1. Introduction

Methods that allow for the synthesis of polymeric nano-sized particles with varied and complex structures and attractive functions have been receiving a great deal of attention during the past decade. This growing interest is due to the fact that optimally designed polymeric nanoparticles ranging in size from 10 nm to 100 nm have many potential benefits in a variety of technologies, including medicine and health [1–4], modifiers for high impact plastics [5], chemical degradation and source recovery [6,7] and so on. Conventional emulsion polymerization is extensively used for the preparation of small particles of polymer latex and coating materials. However, polymeric particles synthesized by this method comprise a quite

large range (eg. 10^1–10^3 nm in diameter), which is not applicable for nanoparticle preparation [8,9]. To improve this system, miniemulsion and microemulsion methods have been developed to prepare particles in the range of 50–200 nm and 20–50 nm, respectively [10,11], with however the requirement of a surfactant concentration in a range of 7–15 wt.% in a water based solvent [12,13]. The addition of a large amount of surfactant in miniemulsion and microemulsion systems may not only increase the production cost, but also be an environmental concern. To overcome these drawbacks, a dropwise addition of monomers into the reactor containing an aqueous solution of emulsifier and initiator was developed [14–23]. The dropwise speed was controlled so that monomer droplets in the reactor would not be formed. As a result, less amount of emulsifier was required to stabilize the growing surface area of the particles; consequently, more micelles are available to participate in the nucleation of new particles, and therefore a larger number of smaller polymer particles

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can be generated compared to the conventional batch process [24–27].

Sajjadi [28] extended the Smith and Ewart [29] theory to study the particle formation under monomer-starved conditions [24], and proposed that:

$$N_P = k\left(\frac{R_I}{R_a}\right)^{\frac{2}{3}}(a_s[S]) \qquad (1)$$

where k is a numerical constant ($0.13 < k < 0.23$), R_a is the rate of monomer addition to the reactor, R_I is the rate of generation of radicals (calculated as $R_I = 2f\,k_d$ [I], with f = efficiency factor of the initiator ($0 \leqslant f \leqslant 1$), k_d is the initiator dissociation rate constant, and [I] is the initiator concentration in the continuous aqueous phase), [S] is the concentration of emulsifier per unit volume of water, and a_s is the area of polymer particle covered by one molecule of the surfactant, which is given in Eq. (2) in terms of Avogadro's number (N_A) and the surface concentration (Γ_1).

$$a_S = \frac{10^{16}}{N_A\Gamma_1} \; (\text{Å}^2/\text{molecule}) \qquad (2)$$

where Γ_1 is given by

$$\Gamma_1 = \frac{\Delta CV}{A_s m} \; (\text{mol/cm}^2) \qquad (3)$$

where A_s is the surface area of the latex (cm^2), V is the volume of the continuous phase, m is the mass of solid adsorbent, $\Delta C = \text{cmc}_P - \text{cmc}$, where cmc$_P$ is the surfactant concentration at which micelles appeared in the diluted latex, and cmc is the critical micelle concentration.

This model assumes that particle formation only occurs in micelles and the rate of particle formation is controlled by the monomer addition rate. In addition, it also assumes that the nucleation rate is proportional to the rate of radical generation and nucleation stops when micelles disappear. According to the expression of Eq. (1), for a given initiator and surfactant, the number of particles (N_P) is inversely proportional to the rate of monomer addition to the reactor (R_a). Herein, a greater number of particles can be produced as the monomer addition rate decreases. In addition, it is clear from Eq. (1) that N_P is also determined by the type of initiator used, and the type and the amount of surfactant supplied. Previous studies [14,19,21–23] have examined the effects of these factors on the particle size by using synthesis of poly (methyl methacrylate) (PMMA) nanoparticles as a model. However, to date, the development of styrene–butadiene rubber (SBR) nanoparticles with sodium oleate as surfactant via the semi-batch DMP method has not been reported in the literature, which is thereby the focus of this study.

2. Experimental

2.1. Materials

Potassium persulfate (KPS, 98%), benzoyl peroxide (BPO,97%), sodium oleate (NaOL, 95%) and *n*-dodecyl mercaptan (*n*-DDM, 98%), were used as received from Sigma–Aldrich. 1,3-butadiene (BD) was purchased from Air Liquid Inc. (95%); styrene (ST) purchased from Sigma–Aldrich

(98%) was washed with 10% sodium hydroxide solution to remove the inhibitor. The treated monomer was further washed with deionized water, and was stored at −20 °C in a refrigerator. The ethanol and tetrahydrofuran (THF) were all reagent grade and used without further purification.

2.2. Apparatus and experimental procedure

The emulsion polymerization was carried out in a Parr series 5100 low pressure reactor (Parr Instruments Moline, IL). The reactor was a cylindrical glass vessel with a round bottom equipped with a four-bladed, paddle-type impeller. In a typical run, the reactor vessel was charged with a desired amount of deionized (DI) water. Emulsifier, initiator and chain transfer agent (if necessary) was dissolved into the DI water to form a continuous phase, which was purged by bubbling pure nitrogen gas (99.99%) for 30 min at room temperature to remove the dissolved oxygen. The continuous phase was then brought up to 50 °C. Subsequently, the copolymerization was started by combining the mixture of BD and ST with the continuous phase in a differential manner via a dropping funnel. The reaction system was kept within 50 ± 0.5 °C with a constant impeller speed of 500 rpm for about 8 h after the completion of the addition of monomers.

The reaction was stopped by dipping the reactor vessel in an ice/water bath. Pure SBR was obtained by precipitation with excess ethanol, washing with DI water, separating with vacuum filtration, and drying under vacuum at ambient temperature for 12 h.

2.3. Particle size and morphology

The average particle size of SBR polymeric nanoparticles was measured by a dynamic light scattering technique (DLS) at ambient temperature. The DLS was equipped with a Microtrac-Nanotrack 150 analyzer (Betatek Inc., Toronto, CA). For each measurement, one to two drops of the sample was diluted to 1 ml with DI water and measured in standard progression with a particle refractive index equal to 1.535.

Confirmation of the SBR nanoparticle size and observation of its morphology were performed under a LEO 912AB 100 kV Energy Filtered Transmission Electron Microscope (EFTEM) (Carl Zeiss Inc., Germany). A 10 μL DI water diluted SBR latex sample was incubated on a 400-mesh copper grid at room temperature. Excess solution was taken away by a piece of tissue paper from the edge of the grid. Latex particles on the grid were stained with 2% (w/v) uranyl acetate for several minutes before the grid was delivered into the TEM chamber for imaging.

2.4. Molecular weight

The molecular weight and polydispersity index (PDI) of the SBR nanoparticles were measured using size exclusion chromatography (SEC, Model 305 TDA, Viscotek, Houston, US), which was calibrated with a polystyrene standard (PS 99 K, $\overline{M}_w = 98251$ and $\overline{M}_n = 96722$, IV = 0.477 in THF at 30 °C). Dried SBR rubber samples were dissolved in THF (reagent grade) and filtered through a syringe filter