Synthesis of highly monodisperse polystyrene microspheres via dispersion polymerization using an amphoteric initiator

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Abstract

The highly monodisperse polystyrene (PS) microspheres were produced by dispersion polymerization using an amphoteric initiator, 2,2′-azobis[N-(2-carboxyethyl)-2-2-methylpropionamidine] (VA-057). The polymerization characteristics were investigated and compared with conventional initiators, 2,2-azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO). The monodisperse PS microspheres having the coefficient of variation (C_v) of diameter all less than 4% are obtained at very low stabilizer, poly(vinyl pyrrolidone) (PVP) concentrations of 1 and 2 wt%. It is found that the size dependence of the VA-057 system, D_n ∝ [VA-057]^{0.267}, is less sensitive than a conventional initiator system. When the same amount, 2 wt%, of AIBN, BPO, and VA-057 is used under the identical PVP concentration of 2 wt%, the D_n/C_v’s are 1.95/11.57, 1.47/22.44, and 2.08 µm/2.50%, respectively. The uniformity of particles was characterized employing an optical analyzer, Turbiscan. For the VA-057 system, the back scattering intensity is linearly reduced with time having a constant sedimentation rate of 48.98 µm/min throughout the settling process. The uniformity of PS particles in the VA-057 system stems from (1) the higher rate of polymerization in early stage of polymerization, followed by significantly faster reduction of the rate, and (2) good dispersion stability of primary particles. Therefore, it is found that the use of an amphoteric initiator, VA-057, is promising for producing monodisperse particles in dispersion polymerization.

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1. Introduction

Recently, micron-sized, monodisperse polymer particles have received much attention because such particles with optimized characteristics can be a good candidate in information technology, electric and electronic application, and biotechnology [1–3]. They are prepared by emulsion, dispersion, or suspension polymerizations. Among those techniques, polymer particles in 1–10 µm with a narrow particle size distribution can be simply obtained by dispersion polymerization in organic media via a single step. The polymer particles grow up from nuclei produced by reaction between initiators and monomer molecules, and then become stable in a spherical shape with aid of polymeric stabilizers [4]. Therefore, the short nucleation period followed by uniform growth of the particles is essential to obtain monodisperse particles in dispersion polymerization.

Dispersion polymerization consists of monomer, initiator, and steric stabilizer and all the components should be dissolved in the polymerization medium such as alcohol. Dispersion polymerization starts in a homogeneous phase, then phase separation occurs when the nuclei precipitate from the medium to give growing particles. Therefore, one of the criteria for choosing the components is solubility in the polymerization medium. Since alcohols such as methanol and ethanol are most frequently adopted as the medium, alcohol-soluble initiators have been naturally chosen. In dispersion polymerization, the most frequently used initiators include azo-compounds such as azobisisobutyronitrile (AIBN), peroxide-compounds such as benzoyl peroxide (BPO), and redox types [5–7] where poly(vinyl pyrrolidone) (PVP) or hydroxypropyl cellulose (HPC) is used as the most common steric stabilizer. In such systems, above...