Preparation of Copoly(styrene/butyl methacrylate) Beads and Composite Particles containing Carbon Black with Hydrophobic Silica as a Stabilizer in Aqueous Solution

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ABSTRACT: A suspension copolymerization of styrene and butyl methacrylate (BMA) in the aqueous phase was conducted at a selected temperature between 65 and 95 °C. Hydrophobic silica was selected as a stabilizer and azobisisobutyronitrile (AIBN) as an initiator. Optimum dispersion of silica in water was obtained at pH 10 while polymerization reaction was run at pH 7. TGA and EDS measurements revealed that 90% of silica functioned as a stabilizer and 10% were incorporated into polymeric particles. Average particle diameter decreased with increasing amounts of stabilizer. Molecular weights displayed an increase when the stabilizer concentration reached 1.67 wt%. An increase in the initiator concentration and/or reaction temperature raised the reaction rate but decreased molecular weights. Particle diameter was nearly independent of the initiator concentration and reaction temperature. An increase in the BMA proportion decreased the glass transition temperature and increased the particle diameter with irregularity in shape. Incorporation of carbon black into the particles composed of styrene and BMA prolonged the reaction time before reaching completion. We have confirmed that a suspension copolymerization of styrene and BMA with hydrophobic silica as a stabilizer can produce spherical composite particles with 1-30 μm in diameter containing carbon black.

Keywords: suspension copolymerization, hydrophobic silica, stabilizer, carbon black, polymer composite particles

I. Introduction

Applications of monodisperse polymeric particles are reaching various scientific fields, such as photonic band crystals,1 lithographic photo masks,2 drug delivery systems,3 size exclusion chromatography4 and adhesives.5 Synthesizing techniques to prepare these particles include emulsion polymerization, soap-free emulsion polymerization and suspension polymerization. The formation of stable aqueous solution depends not only on the wettability and initial placement of polymeric particles but on the interaction between individual particles. Strong hydrophilic stabilizers are usually present in
the aqueous phase, and as a result, they do not provide adequate repulsive power to prevent aggregation of particles. On the other hand, strong hydrophobic stabilizers are placed in the oil phase, reducing the stability of particles in water. Accordingly, the degree of wettability of stabilizers determines the stability of the aqueous solution containing polymeric particles.

Emulsion polymerization usually generates submicron particles whose diameters are in the order of nanometers. To overcome these limitations in diameter Omi et al.6 employed counterion monomers and initiator in seed emulsion polymerization and obtained particles close to 1 μm in diameter. Noda et al.7 increased particle diameters to 2 μm with a nonionic surfactant and a small amount of sodium chloride as a catalyst by emulsion polymerization. Kim et al.8 synthesized polystyrene composite particles in the range of 75 to 950 nm in diameter containing metal stearates by emulsion polymerization. Despite these improvements, emulsion polymerization is more widely used to prepare nano-sized polymeric beads.

On the other hand, studies have been conducted on preparing polymeric beads with diameters ranging between 0.1 and 10 μm by soap-free emulsion polymerization. Since emulsifiers are not used in soap-free emulsion polymerization, it produces particles without emulsifier on the bead surface. In soap-free emulsion polymerization, ionic surfactants forming at the beginning of the reaction function as emulsifiers, enabling simultaneous creation of nucleation, and thus resulting in monodisperse particles.11-15 However, soap-free emulsion polymerization shows limitations in that the stability of the emulsion is highly dependent on the concentration and solubility of monomer and initiator in the water phase. Furthermore, depending on the monomer, particles form only when the concentration of monomer relative to water becomes less than 10% and particle size distribution no longer exhibits monodispersity when particle diameter exceeds 1 μm.16

In a suspension polymerization, Olayo et al.17 reported that an increase in the molecular weight of the organic stabilizer of poly(vinylalcohol) reduced the surface tension of polystyrene particles, resulting in a decrease in particle diameter from 500 μm to 20 μm. On the other hand, there are inorganic stabilizers such as phosphates, sulfates, carbonates and hydroxides.18 Taguchi et al.19 prepared various shapes of calcium carbonates at different temperatures and used these stabilizers in a suspension polymerization of styrene. Calcium carbonates were found to be rectangular when prepared at 20 °C, and dendritic when prepared at 70 °C. Polystyrene beads displayed an average diameter of 1.5 mm after 8 hours of reaction with the former and 400 μm with the latter. Murakami et al.20 reported that hydrophilic poly(vinyl acetate) particles with 1-10 μm in diameter could be synthesized with a stabilizer composed of PVA, borate, and calcium carbonate by controlling the concentration of borate. Shaghaghi and Mahdavian21 investigated the effect of a stabilizer system composed of tricalciumphosphate and sodium dodecylbenzene sulfonate in a suspension polymerization of styrene and found that average particle diameter varied from 74 to 600 μm. Abu-Ayana and Mohsen22 derived new empirical equations correlating the average particle diameter and particle size distribution in the range of 224 to 1240 μm in a suspension polymerization of methyl methacrylate with starch as a stabilizer and benzoyl peroxide as an initiator. Kim. et al.23 reduced the diameter of polystyrene particles to 40 μm containing montmorillonite. Sawatari et al.24 homogenized a mixture of styrene-butyl acrylate monomers and magnetic particles, successfully preparing 5-8 μm composite particles by suspension polymerization.

We reported that polystyrene and poly(butyl methacrylate) particles in the range of 1-30 μm can be prepared with hydrophobic silica.25,26 We made surface modification by carefully controlling the pH of solution. We speculate that careful control of acidity imparts necessary hydrophilicity to hydrophobic silica particles by changing the chemical structure of the surface of silica particles. Based on these observations, we made an attempt to synthesize copolymer particles composed of styrene and butyl methacrylate by suspension polymerization with hydrophobic silica as a stabilizer and water as a reaction medium.

II. Experimental

1. Materials

The styrene and butyl methacrylate monomers and AIBN initiator are the products of Junsei Chemical. The hydrophobic silica, Aerosil R972, is a product of Degussa. The carbon black MA77 was purchased from Mitsubishi Chemical with its diameter 23 nm and BET surface area of 130 m²/g. The water used for polymerization is deionized water from Jeil Distillator. The methanol is an analytical reagent grade from Daejung Chemical and nitrogen is obtained from Sugi Gas Company.

2. Polymerization

Prior to polymerization, phenolic inhibitors in the styrene and butyl methacrylate monomers were removed by washing three times with a 10% sodium hydroxide solution and then three times with deionized water. The AIBN was dissolved into methanol, filtered, vacuum-dried, and then used for polymerization reaction. For the dispersion of silica particles, a selected amount of ammonium hydroxide solution was added to 450 ml of water