Introduction

Polymer particles have a wide range of applications, including standard samples for instrument calibration, column packing materials in chromatography, and micro-electronic materials [1-5]. In particular, monodisperse and size-controlled polymer particles are of interest from both academic and industrial points of view. There are many methods for preparing micron-sized polymer particles. Among them, dispersion polymerization has been used for the past three decades to prepare micrometer-scale monodisperse polymer particles in a single step [6-8].

In dispersion polymerization, steric stabilizers can be divided into homopolymers, macromonomers [9], and block [10] or graft copolymers. The commercial homopolymer stabilizers are poly(N-vinyl pyrrolidone) (PVP) [11,12], methacrylate polymers [13], and various cellulose derivatives [2,14]. It is well known that diblock and triblock copolymers are effective stabilizers in heterophase polymerizations [15]. It can be inferred that amphiphilic block copolymers, in which one segment can anchor to the surface of polymer particles and the other lipophilic segment can extend into the continuous phase, can provide a steric barrier to prevent coagulation of polymer particles. Therefore, control over the molecular weight and molecular weight distribution of block copolymers is important for successful dispersion polymerization. Most block copolymers have been synthesized using meticulous and time-consuming living ionic polymerizations [16], but attempts have been made recently to synthesize block copolymers employing other simple and easy techniques. Among them, controlled/living radical polymerization is a particularly useful technique for the preparation of well-defined polymer structures. The three main techniques capable of inducing living behavior are nitroxide-mediated polymerization (NMP) [17,18], atom transfer radical polymerization (ATRP) [19,20], and reversible addition-fragmentation chain transfer polymerization (RAFT) [21,22].

In this study, controlled poly(styrene-b-4-vinylpyridine) block copolymer was synthesized using the RAFT method and applied to the dispersion polymerization of methyl methacrylate (MMA) as an efficient steric stabilizer.

SHORT COMMUNICATION

Dispersion Polymerization of MMA using Polystyrene-block-poly(4-vinylpyridine) Prepared by a RAFT

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Abstract: Poly(methyl methacrylate) (PMMA) particles were produced through dispersion polymerization using poly(styrene)-block-poly(4-vinylpyridine) block copolymer as a steric stabilizer in methanol. Low-molecular-weight-distribution block copolymers were synthesized using 4-toluic acid dithiobenzoate through a reversible addition-fragmentation chain transfer (RAFT) method. Stable polymer particles were obtained when the block copolymer concentration was 1, 4, or 10 wt% relative to monomer. The average particle size (2.4 – 3.4 µm) varied depending on the concentration of the block copolymer. As the block copolymer concentration increased, the size of the particles decreased. In particular, 4 wt% of the block copolymer produced 2.7 µm monodisperse PMMA (Cv = 3.3 %). The existence of the block copolymer on the PMMA surface was verified through XPS measurements.

Keywords: dispersion polymerization, poly(s-b-4vp), RAFT method, block copolymer

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Experimental Section

The dispersion polymerization ingredients were methyl methacrylate, styrene (Junsei Chemicals, Japan), 4-vinylpyridine (Aldrich, USA), 2,2-azobis(isobutynitrile) (AIBN, Junsei), methanol (Samchun Chemical, Korea), and 4-toluic acid dithiobenzoate (CTA3). CTA3 was prepared using a modification of a procedure described elsewhere [23].

The block copolymer was synthesized using a RAFT method. This polymerization involved two steps; first, PS homopolymer was prepared by bulk polymerization in the presence of styrene (40 mL), AIBN (0.0112 g), and CTA 3 (0.39 g) as a RAFT agent. The solution was sealed and completely sunk into an oil bath at 70 °C. After polymerization, the reaction product was precipitated in methanol and purified through repeated precipitation. A stock solution of PS (1 g), AIBN (0.02 g), 4-vinylpyridine (7 mL), and DMF (10 mL) was prepared under anhydrous conditions. The polymerization process for the preparation of P(S-b-4VP) was the same as that used for the preparation of PS. Dispersion polymerization was performed in a capped scintillation vial with magnetic stirring under a nitrogen atmosphere. Methanol (25 g), methyl methacrylate (2.5 g), AIBN (0.025 g), and various concentrations of the block copolymer were added to the vial. The polymerization temperature was fixed at 60 °C in an oil bath and after completion of the polymerization, the resultant product was rinsed off with methanol.

The chemical structure of the synthesized block copolymer was confirmed by analysis using a Varian 400-MHz 1H-NMR spectrometer with CDCl3 as the solvent. The molecular weight and polydispersity index (PDI) were characterized using a Waters GPC (Gel Permeation Chromatograph). A Hitachi SEM (Scanning Electron Microscope) S-4300 was used to observe the morphology of the PMMA particles. The weight-average diameter (Dw) and coefficient of variation (Cv) were obtained using a Scion Image Analyzer Software by counting 100 of the individual particles from the SEM microphotographs. The surfaces of the PMMA particles were analyzed using an XPS (X-ray photoelectron spectrometer, model ESCALAB 220i-XL); the atomic concentrations were calculated based on the program (spectral data processor, v 4.1).

Results and Discussion

1H-NMR spectra were obtained to confirm the chemical structures of the synthesized PS, P4VP, and P(S-b-4VP). The spectrum of PS displayed the five protons of the phenyl ring in the range 6.1 ~ 1 ppm. For P4VP, two multiplets at 6.1 ~ 5 ppm were observed for the four protons on pyridine ring. The P(S-b-4VP) spectrum showed peaks characteristic of both PS and P4VP, confirming the synthesis of the P (S-b-4VP) block copolymer. The number-average molecular weight and polydispersity index (PDI) of P(S-b-4VP) were 98176 g/mol and 1.28, respectively, and those of the PS block in P (S-b-4VP) were 11388 g/mol and 1.11, respectively. This finding implies that the block copolymer contains a
long poly(4-vinylpyridine) block and a short polystyrene block. The block copolymer dissolved well in methanol, even though methanol is a precipitator of PS. Thus, all of the reaction ingredients dissolved in the medium at the beginning of the reaction and the block copolymer is believed to behave as a stabilizer in the dispersion polymerization.

Figure 1 displays SEM images of the PMMA microspheres prepared by dispersion polymerization in methanol at 60 °C using various concentrations of P(S-b-4VP). By observing the spherical particles, the P(S-b-4VP) was proved to be used as a stabilizer. The average particle sizes varied within the range 2.4-3.4 µm depending on the concentration of the block copolymer. As the block copolymer concentration increased, the PMMA particle diameter decreased; this tendency of decreasing particle size upon increasing the stabilizer concentration has been observed by others [11,14,24,25]. In particular, monodisperse microspheres (2.72 µm; 3.31 % C) were obtained when using 4 wt% P(S-b-4VP). In dispersion polymerization using conventional stabilizers, such as PVP or hydroxylpropyl cellulose (HPC), monodisperse, micron-sized polymer particles result only when using a high concentration of the stabilizer. Typically, the window is 10—3 wt% of stabilizer for styrene and 30 wt% for methyl methacrylate, based on the amount of monomer [3,11,26]. However, our experimental results shows that monodisperse PMMA microspheres were obtained without coagulation or the formation of secondary particles when using as little as 4 wt% of stabilizer. This finding implies that using a small amount of P(S-b-4VP) is more efficient than using a conventional stabilizer, not only for producing PMMA microspheres but also for obtaining them in a very narrow distribution of particle size. Because P(S-b-4VP) consists of hydrophobic PS and hydrophilic P4VP units, we believe that the copolymer molecules are located preferentially on the surfaces of the particles. Therefore, the poly(4-vinylpyridine) segments can provide a steric barrier to prevent coagulation of the polymer particles.

Figure 2 shows the XPS spectrum of the PMMA microspheres prepared using 10 wt% block copolymer for the dispersion polymerization in methanol at 60 °C. Samples for surface analysis were prepared by dispersing the particles ultrasonically in pure methanol. A droplet of the suspension was deposited on aluminum foil and left to dry at room temperature. Two strong peaks appear for carbon and oxygen and a small peak for nitrogen at 280, 520, and 400 eV, respectively. The existence of a nitrogen atom peak implies that the particle surface contains P(S-b-4VP), because nitrogen atoms exist only in 4-vinylpyridine. The atomic concentrations were calculated using a program; the calculated fractions of each element in the PMMA microspheres were 58.1, 36.8, and 5.1 % for carbon, oxygen, and nitrogen, respectively.

In summary, narrow-molecular-weight-distribution amphiphilic block copolymers consisting of hydrophilic 4-vinylpyridine and hydrophobic styrene, using 4-toluic acid dithiobenzoate, were synthesized by a RAFT method. Based on 1H NMR spectra, we confirmed that P(S-b-4VP) was successfully synthesized. This P(S-b-4VP) block copolymer was used as a steric stabilizer for the dispersion polymerization of MMA. As a result, 2.4-4-µm microspheres were obtained when using 1, 4, and 10 wt% of the block copolymer. In particular, when 4 wt% of the block copolymer was used relative to the monomer, a very narrow distribution of particle sizes (2.72 µm; 3.31 % C) was obtained.

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