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Effects of polystyrene-*b*-poly(aminomethyl styrene)s as stabilizers on dispersion polymerization of styrene in alcoholic media

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ABSTRACT

The effects of polystyrene-*b*-poly(aminomethyl styrene) (PS_n-*b*-$PAMS_m$) stabilizers on the particle size (D_n) and size distribution (PSD) in dispersion polymerization of styrene were investigated. The block copolymers, PS_n-*b*-$PAMS_m$, were prepared as follows: (i) atom transfer radical polymerization (ATRP) of styrene (PS-Br), (ii) ATRP of vinylbenzylphthalimide with the PS-Br (PS-*b*-PVBP), and (iii) treatment of the PS-*b*-PVBP with hydrazine. When the dispersion polymerization of styrene proceeded at 60 °C in ethanol with PS_{19}-*b*-$PAMS_{130}$ stabilizer, spherical polystyrene particles with $D_n = 0.91$ µm (PSD $= 1.01$) were obtained. The particle size was strongly affected by the copolymer composition. With an increase in PAMS block length from $m = 54$ to 100 in PS_{17}-*b*-$PAMS_m$, particle diameter became smaller from 1.55 to 0.91 µm. On the other hand, an increase in the length from $m = 20$ to 82 in PS_{34}-*b*-$PAMS_m$s caused an increase in particle size from 0.35 to 0.70 µm. Titration of the particles suggests that 14–81% of stabilizers used in the polymerization system were attached on the polystyrene particle surfaces, depending on the composition of the block copolymers. Thus, for the dispersion polymerization of styrene, PS_n-*b*-$PAMS_m$ block copolymers have both functions as a stabilizer during polymerization and surface-modification sites of polystyrene particles.

1. Introduction

Applications of polymer particles have increased in various fields, such as biomedical analysis, cosmetics, electronics, and chemical industry. In addition to the prime constituent factors including control of particle morphology, size, and its distribution, solvent resistance, strength, surface properties, and productivity are important for these applications. Dispersion polymerization is a useful technique to prepare the micrometer- or submicrometer-scale polymer particles. Particle size and size distribution depend on many reaction parameters of reaction time, temperature, concentration, reaction medium type, and so on [1–11]. In particular, due to the direct participation of stabilizer in the formation of particles, type and concentration of stabilizer are key elements in control of dispersion polymerization. Several kinds of amphiphilic homopolymers such as poly(*N*-vinylpyrrolidone) (PVP) [4–7], poly(acrylic acid) [8], and hydroxypropylcellulose [9–11] have been reported as effective stabilizers.

Block copolymers have also been utilized for dispersion polymerization as stabilizers [12–22]. In a case of an AB type diblock copolymer where the A and B blocks are insoluble and soluble in dispersion medium, respectively, the A block enhances absorption onto particles and the B block provides a protective layer against flocculation. For example, polystyrene (PS) particles have been prepared in alcohol with PS-*b*-poly(ethylene oxide) [13], PS-*b*-poly(vinylacetate-*co*-vinylalcohol) [14], poly(*n*-alkyl methacrylate)-*b*-poly(*N*,*N*′-dimethylaminoethyl methacrylate) [15], polyisobutene-*b*-poly[(4-methyl styrene)-*co*-(4-vinyltriethylbenzyl ammonium bromide)] [16], or PS-*b*-poly(4-vinylpyridine) [17]. In comparison with homopolymer stabilizers, block copolymer stabilizers can provide advantages in the preparation of well-controlled spherical particles: control of particle size by adjusting the composition of block copolymer and enhancement of long-term stability of particles [18]. Although various block copolymers as a stabilizer have been examined in dispersion polymerizations, there are few studies concerning the influence of each block on particle formation.

In this study, PS particles were prepared by dispersion polymerization of styrene in presence of a block copolymer comprising PS and poly(aminomethylstyrene) (PAMS) [23,24], PS_n-*b*-$PAMS_m$ (subscriptions denote the number of repeat units) as a stabilizer. The effects of block copolymer composition as well as stabilizer concentration, temperature, and dispersion medium type on the par-

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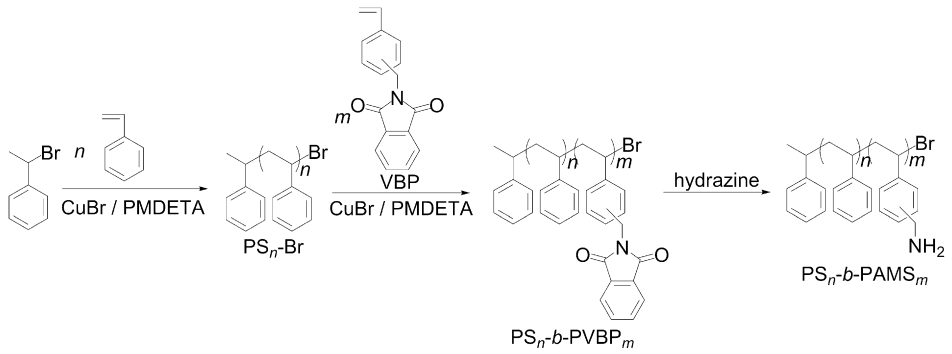

Fig. 1. Synthesis of PS$_n$-*b*-PAMS$_m$.

ticle size and distribution were examined. Furthermore, surface property of the resulting particles was also investigated.

2. Experimental

2.1. Materials

Styrene (Nacalai tesque, 99%), *N*,*N*-dimethylformamide (DMF; Nacalai, 99%), triethylamine (TEA; Wako, 99%), and tetrahydrofuran (THF; Nacalai, 99%) were purified by conventional methods before use. Hydrazine monohydrate (Nacalai, 80%), CuBr (Wako, 95%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA; TCI, 98%), α,α'-azobisisobutyronitrile (AIBN; Nacalai, 98%), anisole (Wako, 95%), and ethanol (Wako, 99%) were used as received. Vinylbenzylphthalimide (mixture of *m*- and *p*-isomers) was prepared as described in a literature [24].

2.2. Characterization

^{1}H (400 MHz) NMR spectra were recorded on a Brucker Avance 400 spectrometer using tetramethylsilane (TMS) as an internal standard with 1 wt% of polymer solution. The gel permeation chromatography (GPC) measurements were carried out on a Jasco–Bowin system (ver. 1.50) equipped with PS calibrated Tosoh TSKgel (G3000H$_{HR}$, G4000H$_{HR}$, and G6000H$_{HR}$) using THF as an eluent. Surface tension measurements were performed by the Wilhelmy plate technique using a Kyowa Kaimenkagaku CBVP-P equipped with an Eyela temperature controlled bath. Scattering electron microscopic (SEM) observation was carried out by a JEOL JSM-5310. Average diameter of particles (D_n) and particle size distribution (PSD) were determined by the following equations

$$D_n = \frac{\sum_{i=1}^{n} D_i}{n}, \qquad D_w = \frac{\sum_{i=1}^{n} D_i^4}{\sum_{i=1}^{n} D_i^3}, \qquad \mathrm{PSD} = \frac{D_w}{D_n},$$

where D_i is diameter of a particle estimated from a SEM photograph and n is the number of particles (=100).

2.3. Titration of the particles

In a typical case, PS particles (50 mg) were added to a 10 mL of 25 mM HCl and sonicated to obtain turbid mixture. The mixture was titrated with 50 mM NaOH, and pH was measured with a Mettler SevenEasy pH meter. From the amount of NaOH consumed between the two equivalent points of free HCl and the protonated amine, aminomethyl styrene units on the particles were estimated.

2.4. Synthesis of PS$_n$-*b*-poly(vinylbenzylphthalimide)$_m$

A typical block copolymer was synthesized as follows. A bromo terminated PS (PS$_{17}$-Br; $M_n = 1700$) was synthesized by atom transfer radical polymerization (ATRP) [25]. A mixture of vinylbenzylphthalimide (5.4 g, 20 mmol), the PS$_{17}$-Br (350 mg, 0.20 mmol), CuBr (30 mg, 0.21 mmol), PMDETA (180 mg, 1.05 mmol), and anisole (13.6 g) was placed into a glass tube, degassed by three freeze-pump-thaw cycles. The glass tube was sealed off under vacuum and placed in an oil bath at 90 °C for 9 h. The reaction mixture was diluted with THF, passed through alumina in order to eliminate CuBr, and then poured into methanol. The precipitant was purified by two times of reprecipitation and thoroughly dried under vacuum, giving a white powder (2.9 g, 48%). Degree of polymerization for poly(vinylbenzylphthalimide) (PVBP) block was determined by ^{1}H NMR on the bases of molecular weight (M_n) of the PS$_{17}$-Br macroinitiator, resulting in PS$_{17}$-*b*-PVBP$_{54}$. Molecular weight distribution (M_w/M_n) was estimated by using PS-calibrated GPC to give $M_w/M_n = 1.10$. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 1.0–2.0 (CH_2–CH), 4.2–4.8 (CH_2–N), 6.0–7.2 (ArH for PS and PVBP blocks), 7.6 and 7.7 (ArH for phthalimide unit in PVBP).

2.5. Synthesis of PS$_n$-*b*-PAMS$_m$

In a typical run, a mixture of the PS$_{17}$-*b*-PVBP$_{54}$ (630 mg) and 80% hydrazine monohydrate (4 mL) was heated at 80 °C for 4 h under stirring. Residual hydrazine was removed by decantation. The product was dissolved in DMF and poured into 5% KOH aqueous solution. The precipitant was filtered, washed with distilled water until pH value became neutral, and thoroughly dried under vacuum at 50 °C, giving PS$_{17}$-*b*-PAMS$_{54}$ as a white powder (350 mg, 90%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 1.0–2.0 (CH_2–CH), 3.6 and 3.8 (*p*- and *m*-benzyl *H*), 6.3–7.2 (ArH for PS and PAMS blocks). Molecular weight of the block copolymer was calculated from the number of repeat units in the corresponding PS$_n$-*b*-PVBP$_m$.

2.6. Dispersion polymerization of styrene

In a typical run, a solution of styrene (526 mg, 5.06 mmol), AIBN (8.3 mg, 0.05 mmol), and PS$_{19}$-*b*-PAMS$_{130}$ (26 mg) in ethanol (4.7 g) in a glass tube was degassed by three freeze-pump-thaw cycles and sealed off under vacuum. Polymerization was performed at 60 °C without any stirring for 17 h. The resulting polymers were filtered over a 0.20 µm membrane filter, repeatedly washed with methanol and deionized water, and dried under vacuum to give PS particles (280 mg, 53%).

3. Results and discussion

3.1. Synthesis of PS$_n$-*b*-PAMS$_m$s

PS$_n$-*b*-PAMS$_m$s were prepared as shown in Fig. 1. Atom transfer radical polymerization (ATRP) of styrene [25] was performed in presence of *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) and CuBr with (1-bromoethyl)benzene as an initiator,