

Synthesis of Poly(styrene-*co*-4-vinylpyridine) Microspheres via Dispersion Polymerization: Effect of the Concentration of 4-Vinylpyridine

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Received 25 January 2008; accepted 4 August 2008

DOI 10.1002/app.29298

Published online 5 December 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Amphiphilic copolymer microspheres of poly(styrene-*co*-4-vinylpyridine) were prepared by dispersion polymerization in an alcohol/water medium. The synthesis of poly(styrene-*co*-4-vinylpyridine) microparticles was successfully carried out, and the latexes had a spherical morphology with good monodispersity. The degree of conversion in the early stage of polymerization decreased with increasing 4-vinylpyridine (4VP) monomer content, but the final conversions were similar (>95%). The copolymerization rate decreased with increasing 4VP content, and a broad

particle size distribution was observed with 20 wt % 4VP because of the prolonged nucleation time. With the 4VP concentration increasing, the molecular weight of the copolymer microspheres decreased, and the glass-transition temperature of the copolymers increased; this indicated that all the copolymers were random and homogeneous. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci*, 111: 2900–2907, 2009

Key words: colloids; copolymerization; dispersions; particle size distribution; polystyrene

INTRODUCTION

Homopolymers and copolymers that contain a pyridine group have attracted significant interest in recent years because of various applications such as amphiphilic block copolymers and coordination reagents for metal nanoparticles.^{1–4} Poly(4-vinylpyridine) (P4VP) is one of the typical basic polymers with a reactive pyridine group, and functional copolymers based on P4VP have been developed. Controlled/living radical polymerization for the 4-vinylpyridine (4VP) homopolymer^{5,6} and block copolymers^{2,7,8} has been reported with various methods. However, the synthesis of micrometer-size monodisperse polymer spheres of styrene and 4VP copolymers by dispersion polymerization has not been reported.

Uniform polymer particles have received much attention in industrial and academic fields because of a wide variety of applications. In particular, accurate control of the polymerization process for preparing monodisperse and size-controlled polymer particles of a well-defined molecular weight has become a highlight of polymer chemistry. The poly-

mer particles can be produced by various heterogeneous polymerizations, including emulsion, suspension, precipitation, and dispersion polymerizations. For the preparation of micrometer-size monodisperse polymer particles, dispersion polymerization has often been used because the procedure is simple and convenient.^{9–16} Despite the disadvantage of using hydrocarbons or alcohols instead of water as the polymerization medium, dispersion polymerization has the unique advantage of producing monodisperse 1–10- μm polymer spheres, which previously were obtained by a time-consuming successive seeding method¹⁷ or a multistage swelling or aggregation process.^{18,19} Such microspheres are being used in electronics, information technology, and biorelated applications.^{20–22}

During dispersion polymerization, an initially homogeneous mixture of a solvent, a monomer, an initiator, and a steric stabilizer nucleates and then grows into the polymer particles.^{9,23,24} The dispersion polymerization occurs in a quite complex manner in particle formation because it is a combination of homogeneous and heterogeneous reaction mechanisms. The solvent is selected to be a poor solvent for the polymer being formed but a good solvent for the stabilizer, which is surface-active, protecting the particles from coalescence by steric stabilization.²⁵ The particles are spherically stabilized by a polymer stabilizer. Thus, the selection of the solvent and

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Contract grant sponsors: Inha University.

stabilizer should be suitably considered. The partitioning of monomers is also a very important factor influencing the particle size, molecular weight of polymer particles, and kinetics of the polymerization process in dispersion copolymerization.

Homopolymers and copolymers that contain a pyridine group such as P4VP have attracted significant interest in recent years because of various applications as amphiphilic block copolymers and coordination reagents for metal nanoparticles.^{26–29} However, the synthesis of microspheres of styrene and 4VP copolymers by dispersion polymerization has not been reported. This study deals with the preparation of monodisperse poly(styrene-*co*-4-vinylpyridine) [P(St-*co*-4VP)] particles with the dispersion polymerization technique. Then, the characteristics of the resultant copolymer particles are investigated in terms of the 4VP monomer concentration.

EXPERIMENTAL

Materials

Styrene (Duksan Pure Chemical, Seoul, Korea) and 4VP (Acros Organics, Geel, Belgium) were purified with an inhibitor-removal column (Aldrich, St. Louis, MO) and stored at -5°C before use. Poly(*N*-vinylpyrrolidone) (PVP; weight-average molecular weight = 40,000 g/mol; Sigma Chemical Co., St. Louis, MO) was used as a steric stabilizer. Ethanol (99%; Samchun, Seoul, Korea) and double-distilled deionized water were used as the polymerization media. 2,2-Azobisisobutyronitrile (Junsei, Tokyo, Japan; 98%) was used as an initiator without further purification.

Polymerization procedure

The dispersion copolymerization of styrene and 4VP was carried out in a four-necked, round glass flask with mechanical stirring at 200 rpm. The composition of the medium was kept constant at an ethanol/water volume ratio of 17/5. A 10 wt % concentration of the monomers (styrene and 4VP) with respect to the medium was charged. The concentration of 4VP was varied from 2 to 20 wt % with respect to the amount of the styrene monomer. The amount of the stabilizer was fixed at 10 wt % with respect to the monomer content. Once the solution in the reactor became homogeneous, it was degassed with bubbling nitrogen gas at room temperature for 30 min. When the temperature of the reaction system was increased to 65°C , 2 wt % initiator, dissolved in a small amount of ethanol at 65°C , was poured into the reactor, and the polymerization was performed for 24 h under a nitrogen atmosphere. During the polymerization, aliquots of the sample

were periodically taken from the reaction vessel for characterization. After completion of polymerization, the resultant product was repeatedly washed with ethanol and water and dried overnight in a vacuum oven at 50°C .

Characterization

The conversion was calculated gravimetrically. A Hitachi S-4300 scanning electron microscope was used to study the morphology of the P(St-*co*-4VP) particles. The number-average diameter (D_n) and the coefficient of variation (C_V) of the particle diameter were defined with the following equations through the counting of at least 100 individual particles from scanning electron microscopy (SEM) microphotographs taken at 10 kV:

$$D_n = \left(\sum n_i d_i / n_i \right) \quad (1)$$

$$C_V = \frac{\left(\sum (d_i - (\sum n_i d_i / \sum n_i))^2 / \sum n_i \right)^{1/2}}{(\sum n_i d_i / \sum n_i)} \times 100 \quad (2)$$

where n_i is the number of particles with diameter d_i .

The particle size distribution was also measured with a particle size analyzer (LS230, Beckman Coulter). The molecular weight and polydispersity index (PDI) were characterized with a Viscotek gel permeation chromatograph. A universal calibration curve was made with 10 polystyrene standard samples (Polymer Laboratories) with molecular weights of 580–7,500,000 g/mol. The P(St-*co*-4VP) copolymer, dissolved in tetrahydrofuran, was injected at a flow rate of 1.0 mL/min. The glass-transition temperature (T_g) of the sample was measured with a PerkinElmer DSC 7. The sample was heated at a rate of $20^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere and quenched and then was reheated for a second run. The T_g was determined at the deflection point in the transition region from the second scan. Turbiscan (Formulation Turbiscan Lab) was employed to investigate the colloidal stability of the particle suspensions. Suspensions in flat-bottomed, cylindrical glass tubes (height of 70 mm and external diameter of 27.5 mm) were placed in the instrument, and the backscattering of light from the suspensions was periodically measured along the height axis at room temperature. The transmission detector received the light going out of the sample at 0° from the incident beam, whereas the backscattering detector received the light scattered by the sample at 135° from the incident beam. The results from transmission are presented as the sedimentation profile, that is, the Δ transmission flux versus time. The backscattering and transmittance of incident light were measured by the calculation of the photon transport mean free

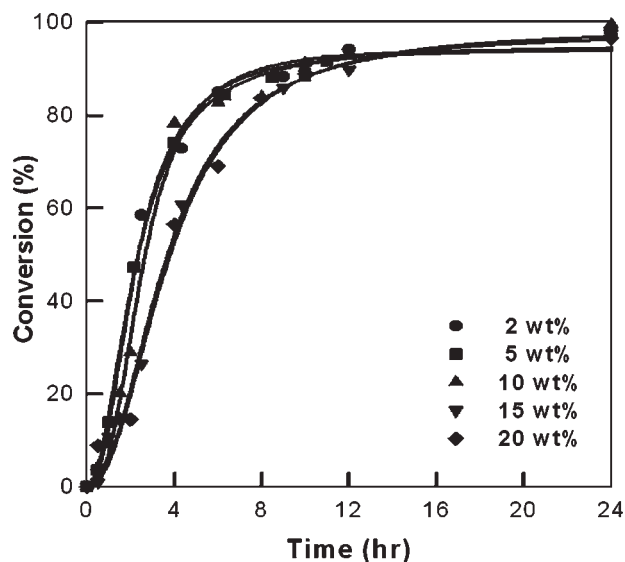


Figure 1 Conversion of P(St-co-4VP) microspheres prepared by dispersion polymerization with various concentrations of 4VP.

path (l^*) throughout the medium. On the basis of Mie's theory, the backscattering and transmittance can be obtained for a concentrated suspension as follows:³⁰

$$\text{Backscattering} \approx (1/l^*)^{1/2} \quad (3)$$

$$\text{Transmittance} \approx \exp(-r/l) \quad (4)$$

where r is the internal radius of the measurement cell and l is the photon mean free path. l^* and l are defined as follows:

$$l^* = \frac{2d}{3\Phi(1-g)Q_s} \quad (5)$$

$$l = \frac{2d}{2\Phi Q_s} \quad (6)$$

where d , Φ , g , and Q_s denote the mean particle diameter, volume fraction of the dispersed phase, asymmetry factor, and scattering efficiency factor, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the conversion of styrene and 4VP monomers into P(St-co-4VP) copolymers by dispersion polymerization with various 4VP concentrations. The degree of conversion in the initial stage decreased with the 4VP monomer concentration increasing, but the final conversions at 24 h were similar (>95%) for all 4VP concentrations. The lines in Figure 1 were achieved by the curve fitting of the experimental data with commercial software (Sigma-

Plot). Then, the polymerization rate was calculated with the first derivative of each curve. Figure 2 presents the effect of the 4VP concentration on the polymerization rate of P(St-co-4VP) copolymers. In the early stage, the polymerization rate increased with time because of the nucleation and then reached a maximum. After that, the polymerization rate decreased with time. This trend is characteristic of radical polymerization. Comparing the slopes of the lines in Figure 2, we found that the copolymerization rate of styrene and 4VP decreased with an increase in the 4VP monomer concentration, and the polymerization rate of 4VP was lower than that of the styrene monomer. It has also been reported that the polymerization rate of 4VP is lower than that of the styrene monomer in nitroxide-mediated living radical polymerization.⁸ The maximum polymerization rate was observed at a 4VP concentration of 5 wt %, and the peak polymerization rate decreased with the 4VP concentration increasing.

The particle size distributions of P(St-co-4VP) copolymers prepared by dispersion polymerization with various concentrations of 4VP are shown in Figure 3. Monodisperse micrometer-sized copolymer particles were obtained for all 4VP concentrations. However, a broad particle size distribution was observed at 20 wt % 4VP because of a decreased polymerization rate. In dispersion polymerization, all reaction ingredients are dissolved in the medium, in which particles are generated from the oligomeric species, and microspheres subsequently grow by the adsorption of oligomers and monomers from the medium. Dispersion polymerization proceeds through two stages:²³ (1) a very short nucleation

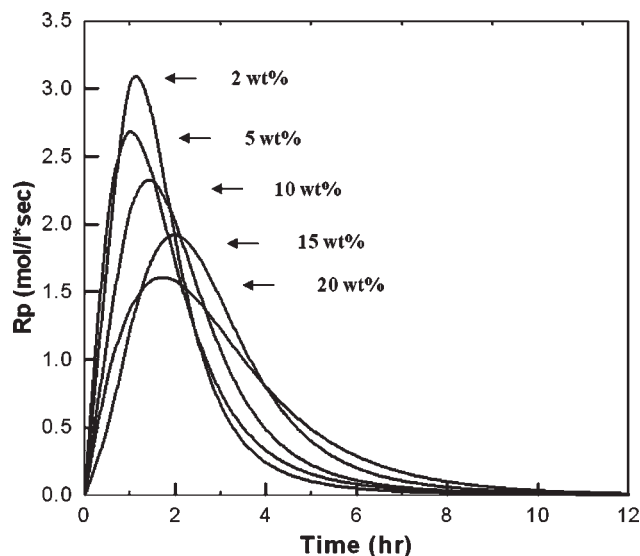


Figure 2 Effect of the 4VP concentration on the rate of polymerization (R_p) of P(St-co-4VP) microspheres by dispersion polymerization.

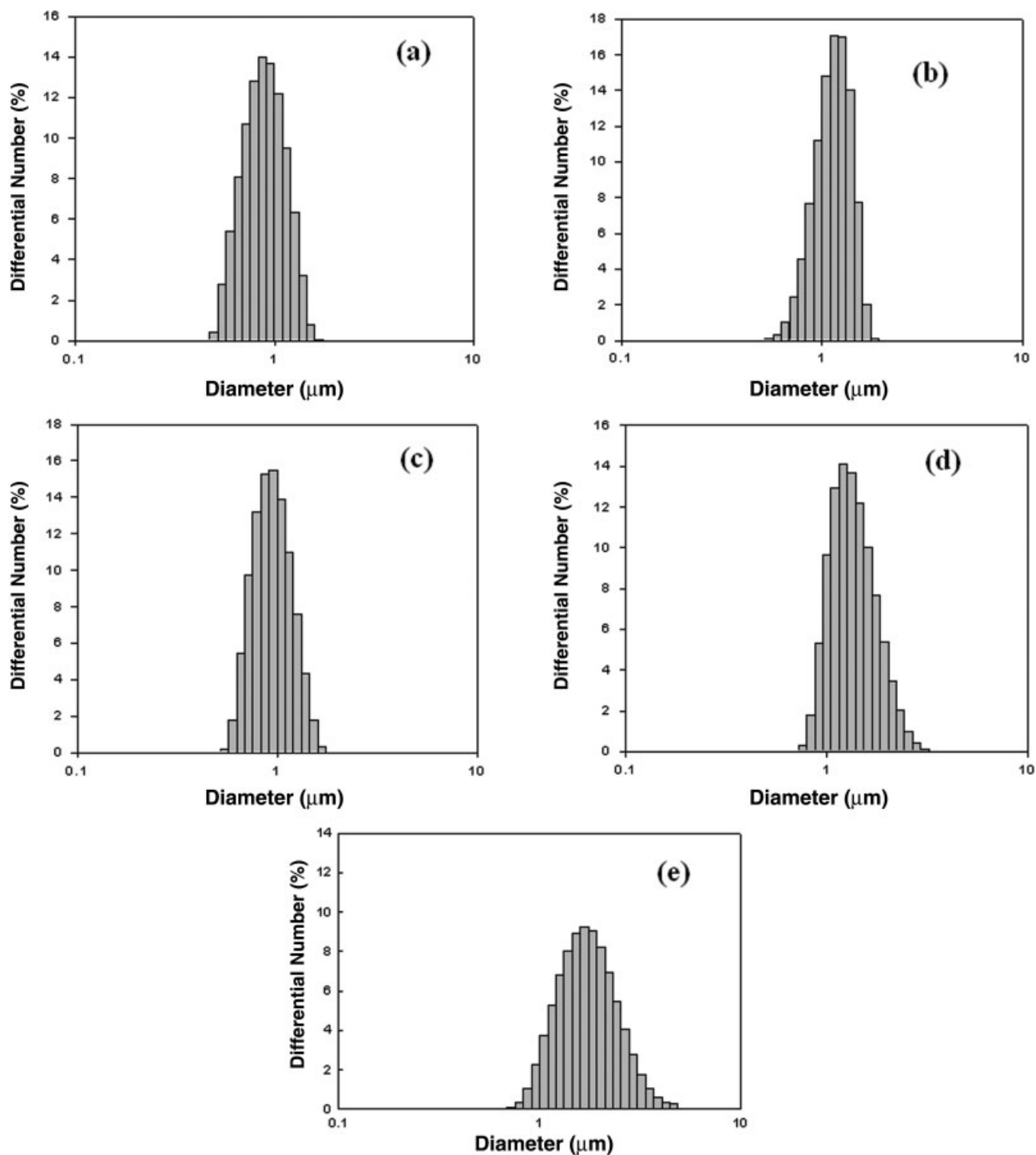


Figure 3 Particle size distribution of P(St-co-4VP) microspheres with various amounts of 4VP: (a) 2, (b) 5, (c) 10, (d) 15, and (e) 20 wt % with respect to the amount of the styrene monomer.

stage in which the primary particles are formed through coagulation and (2) a growth phase in which the number of particles stays constant. In the latter stage, the surfactant covers the particles so that sufficient steric stabilization prevents further coagulation. The particle number and particle number distribution are determined by the nucleation stage if no secondary particles or coagulum is

formed during the particle growth stage. For the final particles to be uniform in size, a short nucleation period and uniform growth of those primary particles are necessary.^{10,23} Among these factors, the nucleation stage plays a key role in determining the final particle size and its distribution. In this experiment, the broadening of the particle size distribution was observed at 20 wt % 4VP, possibly because of

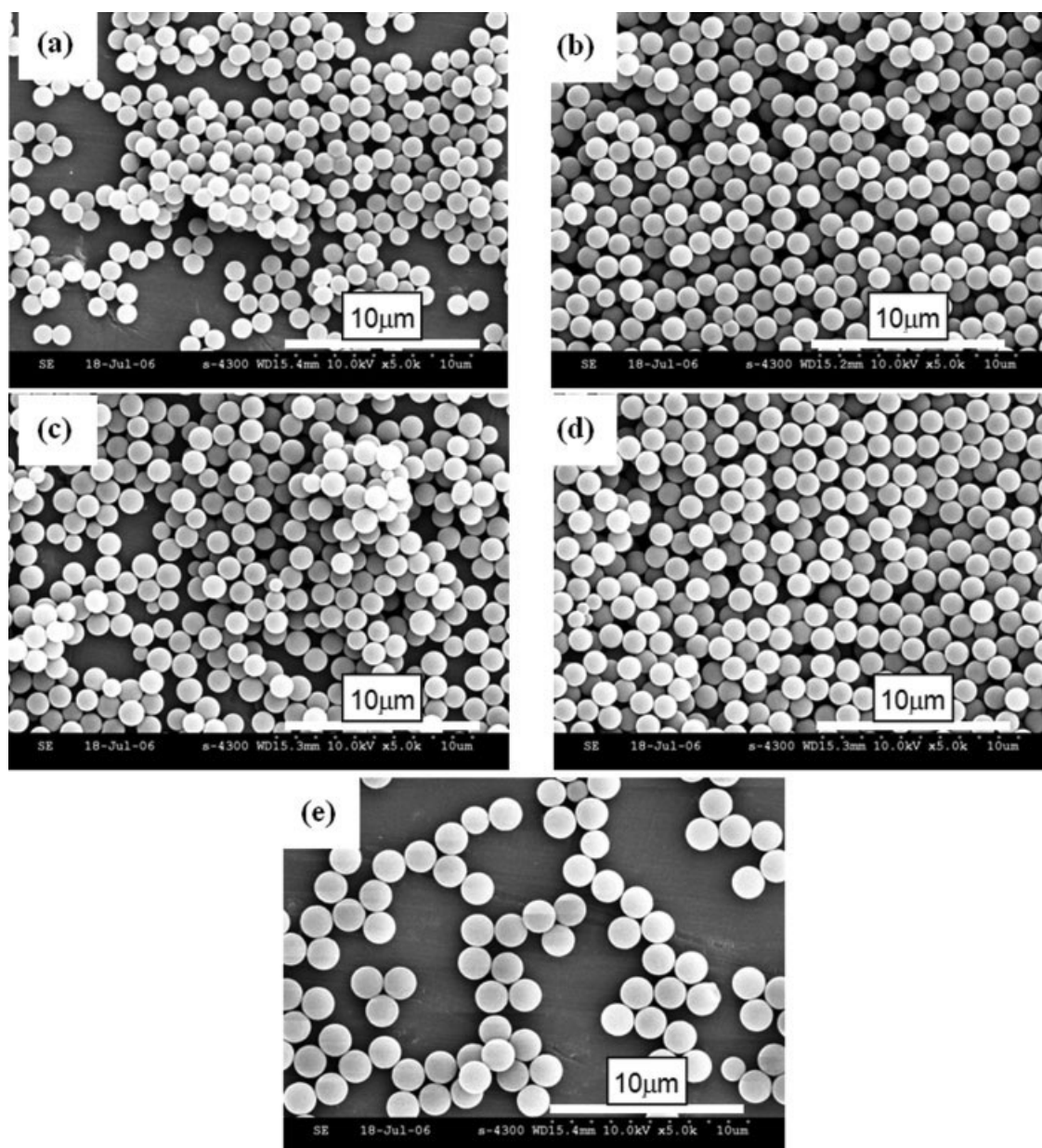


Figure 4 SEM microphotographs of P(St-co-4VP) microspheres with various concentrations of 4VP: (a) 2, (b) 5, (c) 10, (d) 15, and (e) 20 wt % with respect to the amount of the styrene monomer.

the prolonged nucleation time with the decreased polymerization rate.

Figure 4 shows SEM photographs of P(St-co-4VP) copolymer particles prepared by dispersion polymerization with various 4VP concentrations. It shows that the synthesis of P(St-co-4VP) copolymer microparticles was successfully carried out, and all the latexes had a spherical morphology with good monodispersity. The image of copolymer particles with 20 wt % 4VP was prepared by repeated washing with ethanol and water to completely remove residual PVP molecules in the medium. The characteristics of Figure 4 are analyzed and plotted in Figure 5, which shows the relationship between D_n and

C_V along with the 4VP concentration. As the 4VP monomer concentration increased, the size of the P(St-co-4VP) copolymer microparticles tended to increase because of the decreased polymerization rate. The ultimate size of particles is determined by the number of nuclei formed in the very early stage of polymerization. The nuclei are generated by the precipitation of oligomeric species whose molecular weight exceeds the critical solubility limit in the reaction medium. At a low polymerization rate, a lower number of nuclei are generated in the early stage of polymerization, and thus the particle size is increased. Because of the prolonged nucleation time, C_V was also higher for 15 and 20 wt % 4VP. The

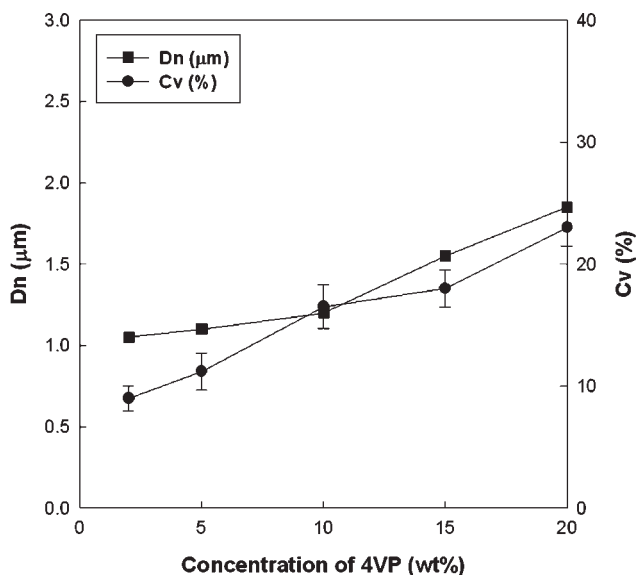


Figure 5 D_n and C_v of P(St-*co*-4VP) microspheres with various concentrations of 4VP.

lower the rate of polymerization was, the higher C_v was of the microparticles.

The molecular weight evolution and PDI of P(St-*co*-4VP) copolymers with respect to the amount of 4VP monomer are presented in Figure 6. The molecular weight decreases with increasing 4VP concentration because of two factors: the termination rate constant and the particle size. Because 4VP has a higher termination rate constant (33 L/mol s) than styrene (10.5 L/mol s),³¹ the termination reaction is pronounced with a larger amount of 4VP, and this results in the decrease in the molecular weight. It is typically observed that there is an inverse relationship between the molecular weight and size of polymer particles in dispersion polymerization.⁹ The

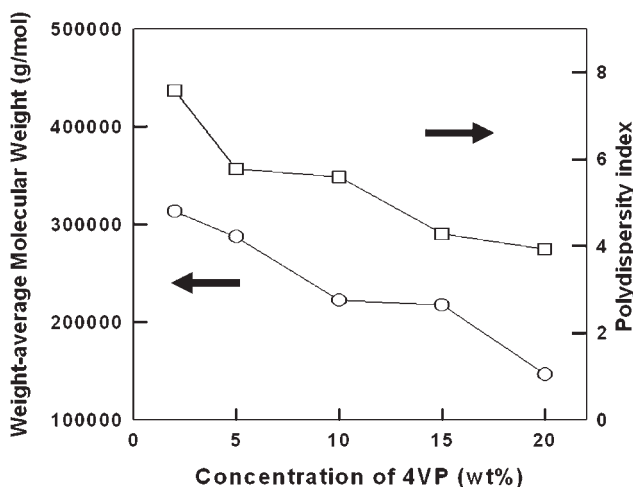


Figure 6 Molecular weight and PDI of P(St-*co*-4VP) microparticles prepared by dispersion polymerization with various concentrations of 4VP.

smaller the particles are, the higher the molecular weight is. This phenomenon has been ascribed to the suppressed termination reaction in the particle phase due to the high viscosity of the monomer/polymer particle medium, which more significantly occurs in small particles. Furthermore, oligomer capture more readily occurs for small particles because of their greater surface area, which gives a higher molecular weight.¹² In addition, the corresponding decrease in the molecular weight and PDI value is caused by the decreased polymerization rate due to the increasing 4VP concentration. Also, the molecular weights of copolymer microspheres are unusually high in dispersion polymerization. It has been reported that a higher experimental molecular weight results from the grafting of PVP stabilizers with polymer particles because dispersion polymerization is initiated on the stabilizer molecules by the abstraction of labile hydrogen.³² The PVP stabilizer generally used in the dispersion polymerization is not only physically adsorbed onto the particle surface but also chemically bound by forming a covalent bond with the monomer.²⁴ Because of the chemical attachment of the PVP stabilizer onto the copolymer molecules, a significantly high molecular weight of poly(St-*co*-4VP) copolymer microspheres was obtained during the dispersion polymerization.

To investigate the copolymer chain structure, T_g may provide some clues about the structure of the copolymers. T_g was determined with differential scanning calorimetry measurements. Figure 7 shows T_g of the P(St-*co*-4VP) copolymers prepared with various concentrations of 4VP. T_g of polystyrene is 100°C, and T_g of P4VP is 144°C. The results from differential scanning calorimetry indicate that all the synthesized

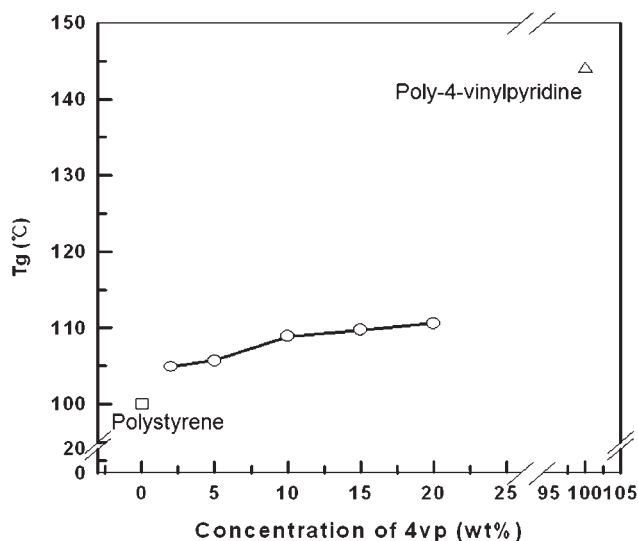


Figure 7 T_g of P(St-*co*-4VP) copolymer particles prepared by dispersion polymerization with various concentrations of 4VP.

copolymers had only one glass transition (ranging from 105 to 115°C), and T_g of the copolymers increased with the 4VP concentration increasing; this indicated that all the copolymer microspheres prepared by dispersion polymerization were possibly random and homogeneous.

Turbiscan was successfully employed in this study to investigate the sedimentation behavior of the P(St-co-4VP) microspheres as a measure of the colloidal stability of the particles. Dispersion destabilization phenomena, including particle size variation kinetics such as coalescence or flocculation and particle

migration kinetics such as creaming or sedimentation, can be readily investigated with Turbiscan.^{16,33–35} The sedimentation behaviors of P(St-co-4VP) microspheres suspended in ethanol were monitored every 1 h, and a backscattering intensity profile versus the height in the sample is shown in Figure 8. The P(St-co-4VP) particles with 15 wt % 4VP [Fig. 8(d)] showed poor dispersion stability. Because the particles precipitated from the top layer, the concentration of particles gradually decreased at the top, and this permitted more light to transmit through the sample. This caused a stepwise decrease in the

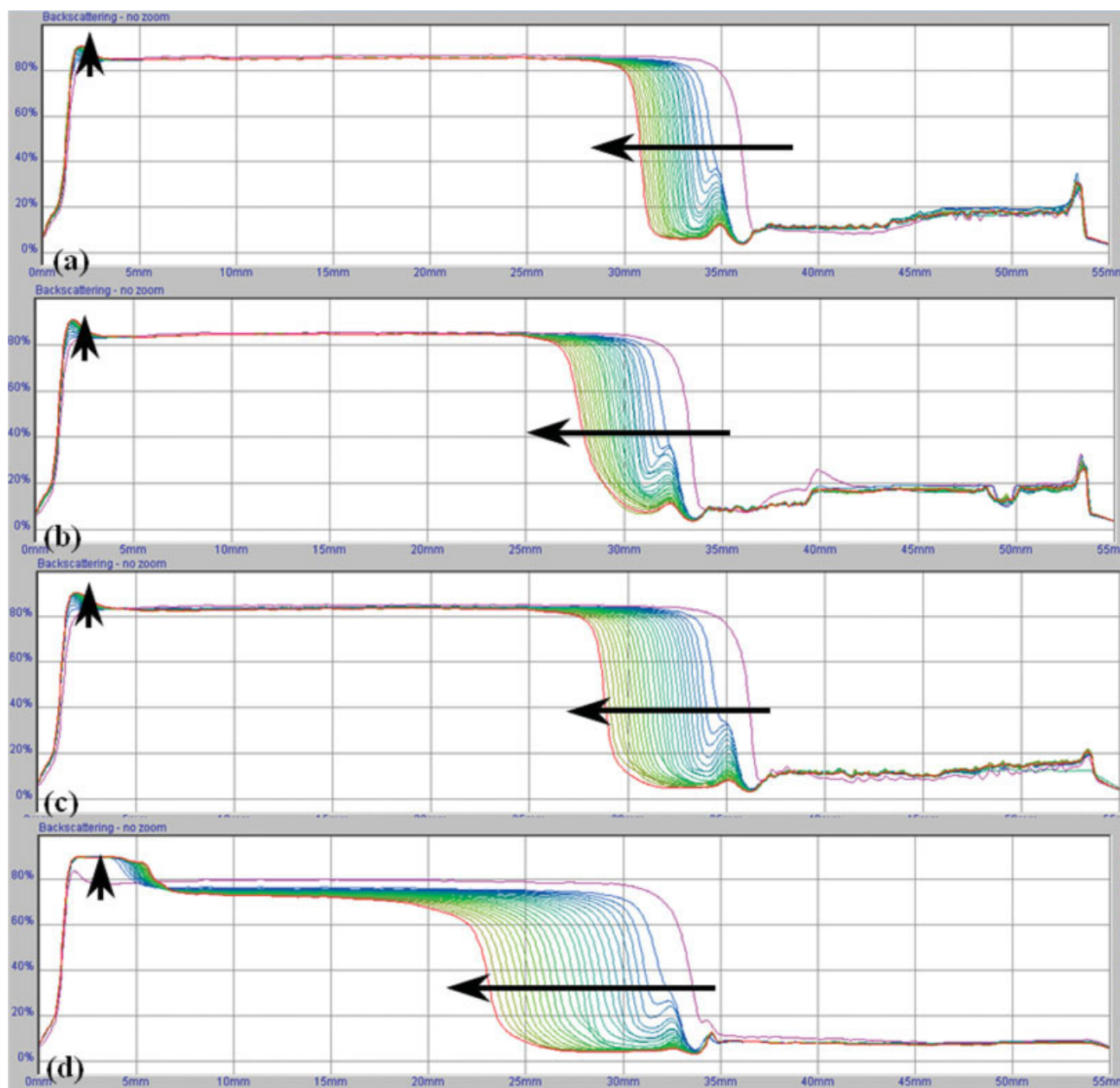


Figure 8 Backscattering intensity (y axis) profiles along the sample height (x axis) were measured every hour. The P(St-co-4VP) particles were suspended in ethanol at room temperature. The particles were produced with different concentrations of 4VP: (a) 2, (b) 5, (c) 10, and (d) 15 wt % with respect to styrene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

