Size Control of Polystyrene Beads by Multistage Seeded Emulsion Polymerization

SANG-EUN SHIM,² YOON-JONG CHA,³ JAE-MAN BYUN,⁴ SOONJA CHOE¹

¹ Department of Chemical Engineering, Polymer Science and Engineering Research Institute, Inha University, Inchon 402-751, Korea

² School of Engineering, University of Akron, Akron, Ohio

³ Technical Research Center, Baec-San Ltd., Ansan, Korea

⁴ Technical Research Center, Orient Chemicals, Ansan, Korea

Received 6 April 1998; accepted 17 September 1998

ABSTRACT: Micron-sized monodisperse crosslinked polystyrene (PS) beads have been prepared by a multistage emulsion polymerization using styrene monomer, divinylbenzene crosslinking agent, and potassium persulfate initiator in the absence of emulsifier. In the first stage of the reaction, the lower the reaction temperature, the larger the bead size obtained. In the later stages of the reaction, the particle size is increased with the initiator concentration and monomer content. Particle nucleation of the preexisting polymer seed of 0.7–0.8 μ m in diameter is prepared at 60°C, then the monodisperse crosslinked PS beads > 2 μ m are synthesized up to the third stage of the reaction. As the particle size grows, the number of free radicals in the growing particles increases, and the conversion of the next stage is continuously increased. The reaction mechanism is suggested that the continuous polymerization be conducted due to the diffusion of monomer into the preexisting particles to induce spherical beads in the later stages of the reaction. Otherwise, phase separation or the formation of protrusion by the capture of free radicals will be taking place. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2259–2269, 1999

Key words: micron-sized beads; monodisperse crosslinked PS beads; multistage seeded emulsion polymerization; reaction mechanism

INTRODUCTION

Recently, we reported the preparation procedure of crosslinked monodisperse polystyrene (PS) beads by emulsion polymerization in the absence of emulsifier and the mechanical properties of SBR composites filled with polymer beads.¹ The polymer beads crosslinked with 10 mol % divinylbenzene (DVB) at 80°C were uniformly prepared in the early stage of the reaction and gradually grown with the reaction time. However, one of the limitations of emulsion polymerization is the formation of particle size smaller than 1 μm in a single stage of the reaction.^{1–5}

Ugelstad and colleagues⁶ developed the preparation method of micron-sized monodisperse particles using two steps of swelling technique in the presence of an emulsifier to prevent a formation of coagulum or secondary small particles during the seeded emulsion polymerization. The efficient method they proposed requires a long period of time in the swelling process and is difficult to carry out. To prepare micron-sized monodisperse spheres, it is necessary to use seed particles pre-

Correspondence to: S. Choe.

Journal of Applied Polymer Science, Vol. 71, 2259–2269 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/132259-11

No. of	Sturono	DVB	KDS	Wator
NU. UI	Styrelle		(07)	(m)
Steps	(g)	(g)	(%)	(g)
Series 1: 1st s	stage			
1	9.2	0.8	0.25	100
2	9.2	0.8	0.5	100
3	9.2	0.8	1	100
4	9.2	0.8	1.5	100
Series 2: 2nd	stage			
1	10	1	0.25	40
2	10	1	0.5	40
3	10	1	1	40
4	10	1	1.5	40
Series 3: 2nd	stage			
1	20	2	0.25	113.3
2	20	2	0.5	113.3
3	20	2	1	113.3
4	20	2	1.5	113.3
Series 4: 2nd	stage			
1	30	3	0.25	186.7
2	30	3	0.5	186.7
3	30	3	1	186.7
4	30	3	1.5	186.7
Series 5: 1st-	3rd stages			
1st stage	9.2	0.8	0.5	100
2nd stage	30	3	2	186.7
3rd stage	30	4.5	2	100.8

Table IRecipes of Experimental Series forEach Step

pared by emulsion polymerization and enlarge them up to the desired size in the further stages of reactions. Seeded polymerization has been conducted for several decades, and various mechanisms have been proposed for the growth of latex particles. Grancio and Williams⁷ suggested that the growing particles consist of an expanding polymer-rich core surrounded by a monomer-rich shell, with the outer shell providing a major locus of polymerization. Chung-li and colleagues⁸ found that the swelling rate of the preformed latex particles was too low to account for the rate of particle growth. Therefore, a heterocoagulation mechanism was proposed, in which coagulation of polymer particles formed onto the seed particles and played an important role in particle growth. The capture mechanism of a free radical has been developed by Fitch and Shin,⁹ Kao and colleagues,¹⁰ and Goodall and colleagues,¹¹ based on the mechanism proposed by Smith and Ewart.¹² In this model, sulfate-free radicals, generated by the decomposition of persulfate initiator, react with styrene monomer dissolved in the aqueous

phase to form oligomeric free radicals.¹¹ The mechanism of radical capture is still a debated issue.

In this article, we designed a modified seeded emulsion polymerization to control the bead size, in which the reaction reagents were added before the conversion was not completely performed. This is the first method to prepare the micronsized polymer particles using multistage seeded emulsion polymerization in the absence of emulsifier. Then, the reaction mechanism for this procedure has been proposed.

EXPERIMENTAL

Materials

Technical grade styrene monomer and DVB (55% *p*-DVBs and *m*-DVBs, 42% ethylbenzenes, and 3% diethylbenzenes) were purchased from Aldrich Chemical Co. and washed with deionized water after the 10% aqueous sodium hydroxide solution washing for four times to remove the inhibitor. Potassium persulfate (KPS) was purchased from Aldrich Chemical Co. and used without further purification. Deionized water was used throughout the polymerization process.

Synthesis of PS Beads in the First Stage

Throughout the first stage of the reaction, preliminary study of the experimental conditions (such as temperature, reaction recipe, reaction time, stirring speed, etc.) has been conducted to control the monodisperse micron-sized particles. Crosslinked PS beads are prepared by an emulsion polymerization using styrene monomer, DVB crosslinking agent, and an adequate amount of KPS in the absence of an emulsifier. The synthetic process modified in our laboratory is as follows. Polymerization was conducted in a 700-mL reaction flask by mechanically stirring under a nitrogen atmosphere. Deionized water was added to the reaction flask. Nitrogen is bubbled in the flask and continued throughout the reaction. Prewashed styrene and DVB with an aqueous solution of sodium hydroxide were added to the flask and allowed to mix for 20 min to equilibrate. Then, KPS dissolved in 50 mL of water, was added. The ratio of DVB to monomer was controlled to 0.5-15 mol %. Polymerization was conducted at 350 rpm, and temperature varied in the range of 60°-80°C. After the reaction, the







Figure 1 SEM microphotographs of PS beads crosslinked with 0.5 mol % DVB at various temperatures (°C): (a) 60, (b) 70, and (c) 80.

flask was removed from the water bath, then the latex of PS beads in water was poured into a 1000-mL steel bottle and cooled at -15° C for 8 h. As the frozen latex was melted at room temperature, two phases of water and polymer particles were separated, then isolated by filtration using glass filter. To remove moisture and unreacted monomer, the wet beads were dried in a vacuum oven at 60°C for 24 h and yielded a fine white powder.

Preparation of Micron-Sized PS Beads

Since the lower the reaction temperature, the larger the particle sizes were obtained at the first stage, the beads prepared at 60° C were used for further reactions.

A desired amount of seed latex remaining in the reactor is used for a subsequent stage reaction. Warm deionized water preheated at the reaction temperature, styrene, and DVB were



Figure 2 Conversion of PS beads crosslinked with 0.5 mol % DVB and 0.5 wt % initiator at various temperatures (°C): (\bullet) 60, (\blacksquare) 70, and (\blacktriangle) 80.

added into the reactor under a nitrogen atmosphere, which was containing the preformed seed latex and remaining reagents. After 30 min, aqueous initiator solution was added, and the reactants were stirred for the desired period of time at the selected temperature. This procedure was repeated for a subsequent stage of polymerization. Addition of persulfate at each stage is required to lead a rapid polymerization and to sustain the reaction.

A large amount of monomer (from one to three times) was added in the second stage of the reaction, and initiator content was increased from 0.25 to 1.5 wt % to investigate the effect of monomer and initiator contents on the particle size and size distribution. The ratio of DVB content to monomer was fixed to 8, 10, and 15 mol % at the first, second, and third stages, respectively. Experimental recipes used at each stage are listed in Table I. The solid content, which is the ratio of the monomer and DVB over water, is controlled to be 10, 15, and 20 wt % for the first, second, and third stages of the reaction, respectively. DVB content is controlled by the amount of monomer, and KPS is the weight percent of the total content of styrene and DVB.

Series 1 directs the first stage of the reaction to prepare latex seeds with various concentrations of KPS. According to steps 1–4 in series 1, the concentrations of KPS are increased from 0.25, 0.5, 1, to 1.5%. For series 2–4, which belongs to the second stage of the reaction, the seed particles used are prepared by the recipe of no. 2 of series 1. In series 5, the amount of the reagents is followed in Table I, where styrene and water contents are controlled to be 10, 15, and 20% at the first, second, and third stages, respectively.

After the reaction, the product is easily separated by filtration and dried in a vacuum oven at 80°C.

Analysis

To investigate the size, size distribution, and morphology of the beads, a drop of PS beads diluted with an equal amount of methanol was placed on a cover glass and dried with clean air at room temperature. The dried beads were coated with gold and palladium using a sputter coater, and morphology of the beads was studied using a Phillips SEM-515. Size and distribution of swollen beads were also measured by a dynamic light scattering (DLS) method by the next procedure. A test tube was washed by deionized water and dried at a vacuum oven for 1 day. Synthetic PS beads were dissolved in 0.005 wt % tetrahydrofuran solution at room temperature for 24 h, then the solution poured into a test tube. DLS measurements for the beads was accomplished using a Marlvern Instrument 4700 type.

RESULTS AND DISCUSSION

Figure 1 shows the effect of the reaction temperature on the bead size crosslinked with 10 wt %styrene, 0.5 mol % DVB, and 0.5 wt % KPS at 60°C for 28 h, 70°C for 18 h, and 80°C for 9 h, respectively. Polymerization was conducted at the temperature above 60°C for the purpose of adequate rate of initiator decomposition. Bead size was ordinarily measured at maximum conversion, \sim 100%. In all cases, the lower the reaction temperature, the larger the PS beads were observed with monodisperse distribution. As shown in Figure 1, bead size prepared at 60° C was ~ 700 nm, whereas that at 80°C was \sim 429 nm. The monomer with a low aqueous solubility, such as styrene, may exhibit sensitive dependence of the bead size on the polymerization temperature.^{13,14} The temperature of polymerization affects the equilibrium concentration of the monomer in the aqueous medium. The higher the monomer concentration by raising the temperature, the more oligomers are formed with an appearance of small growing particles. Thus, the particle size is reduced with temperature, which is one of the vari-









Figure 3 SEM microphotographs of PS beads prepared at the first stage with different initiator concentrations: (a) series 1, no. 1; (b) series 1, no. 2; (c) series 1, no. 3; and (d) series 1, no. 4.

ables controlling the particle size in emulsion polymerization.

To enlarge the monodisperse bead size at successive stages of the seeded polymerization, the

polymerization temperature was fixed at 60°C. The conversion of PS beads crosslinked with 0.5 mol % DVB, 10 wt % styrene, and 0.5 wt % KPS at $60^{\circ}-80^{\circ}$ C is plotted in Figure 2. The rates of poly-



Figure 4 Size distributions of series 1 with various initiator concentration at 60°C: (\blacksquare) 0.25 wt %, (\bullet) 0.5 wt %, (\bullet) 1.0 wt %, and (\bullet) 1.5 wt %.

merization increase with the reaction temperatures due to the high rate of initiator decomposition or propagation. As the reaction was progressed, the beads became monodisperse and their sizes gradually increased, then leveled off. Free radicals from the initiators are formed in the aqueous phase and, at the beginning of the reaction, proceeded polymerization by reacting with monomer dissolved in water. Micelles are not likely to form by alignment of oligomeric free radicals. Instead, termination of the radicals will occur forming dead oligomers that may or may not participate in the formation of micelles. It is unlikely that two radicals could be present in a micell without instantaneous termination occurring. In the beginning of the reaction, of which conversion reaches $\sim 10\%$, the number of growing particles is fixed at the interval II of the Smith-Ewart theory,¹² where particle nucleation does not occur any more, and the rate of polymerization is constant with time. Then, the bead size increases as the monomer continues to migrate from the monomer droplet, through the aqueous phase, into the swollen polymer particles (latex particle). Because the emulsion polymerization is conducted in the absence of an emulsifier, surface active oligomeric radicals formed in the aqueous phase are adsorbed onto the surface of the growing particles and stabilize the particles.

Figures 3 and 4 show the size and size distribution of the beads crosslinked with 8 mol % DVB and various concentrations of initiator (0.25–1.5 wt %) at 60°C obtained by scanning electron microscopy (SEM) and a light scattering method, respectively. D_n , D_w , and D_z where the number, weight, and z average diameter of the particles can be calculated by the following equations,

$$D_n = rac{\sum n_i d_i}{\sum n_i} \qquad D_w = rac{\sum n_i d_i^4}{\sum n_i d_i^3} \qquad D_z = rac{\sum n_i d_i^5}{\sum n_i d_i^4}$$

where n_i is the intensity of the particle size distribution, and d_i is the diameter of the particle. Uniformity of the particle is used to calculate the following equation.

Uniformity
$$= \frac{D_w}{D_n}$$

The values of D_n , D_w , D_z , and Uniformity are listed in Table II. This result shows that the number of bead size (D_n) is decreased from 925.1 nm to 793.3 nm, with the increased initiator concentration from 0.25 wt % to 1.5 wt % and the D_w and D_z as well. The D_n measured by DLS and SEM are comparable in Table II. The slightly larger dimension of the beads by DLS, which is raised from the swelling effect by solvent, is analogous to that observed by SEM. Variations in initiator concentration have a small effect on particle size. The particle size distribution is monodisperse in the range between 1.0371 and 1.0079.

Table II Various Sizes and Uniformity of Series 1 with Different Initiator Concentrations Measured by DLS (D_n, D_w, D_z) and SEM

No.	D_n (nm)	SEM (nm)	D_w (nm)	D_z (nm)	Uniformity
1 (0.25 wt %)	925.1	810	959.4	967	1.0371
2 (0.50 wt %)	879.2	789	911.2	922	1.0376
3 (1.00 wt %)	845.5	720	877.5	889	1.028
4 (1.50 wt %)	793.3	716	799.6	802	1.0079



Figure 5 Conversion of PS beads prepared at each stage: (\blacktriangle) first stage, PS beads with 8 mol % DVB; (\blacksquare) second stage, PS beads with 10 mol % DVB; and (\bullet) third stage, PS beads with 15 mol % DVB.

Figure 5 depicts the conversion of the beads prepared by three stages of the reaction in series 5 listed in Table I. The conversion was calculated according to the following equation by gravimetric analysis,

Conversion (%) =
$$\frac{W_{ds}}{[W_{mo}/(W_{wa} + W_{mo})] \times W_{sa}} \times 100$$

where W_{ds} , W_{mo} , W_{wa} , and W_{sa} are the weight of the dried polymer latex, fresh monomer, water, seed latex, and latex sample, respectively. The overall conversion was increased with the reaction stages.

Preliminary study for controlling the bead size has been conducted, and the morphologies of the beads obtained from the second step at 60°C are depicted in Figure 6. The recipe is not shown in Table I. DVB (2 mol %) was used in the first stage for 16 h, followed by a successive process of polymerization with 5 mol % DVB for 24 h at the second reaction stage. The amount of DVB was controlled in the second stage to minimize the formation of protrusion and indentation after collision between the particles. As seen in this figure, the bead size is 0.9 μ m in the first stage, then grown to 1.8 μ m at the second stage. Moreover, SEM microphotographs of the beads show fairly monodisperse distribution. It is suggested that, in successive stages of seeded polymerization, the secondary nucleation





Figure 6 SEM microphotographs of PS beads prepared by seeded polymerization at 60°C: (a) first-stage latex particles of PS with 2 mol % DVB (bead size: 0.9 μ m); and (b) second-stage latex particles of PS with 5 mol % DVB (bead size: 1.8 μ m).



Figure 7 SEM microphotographs of PS beads at the second stage: (a) series 2, no. 1; (b) series 3, no. 1; and (c) series 4, no. 1.

of the preexisting seed particles compete with the primary nucleation that induces formation of new growing particles. Because styrene has extremely low solubility in water, primary nucleation by micellization mechanism is not so favored as the (secondary) nucleation on seeds. Oligomeric free radicals would be captured by the large seed particles rather than forming micelles or initiating new particles. As a result, a unimodal distribution of large particles is reached. Polymerization is continued to form spherical particles around the bead surface. However, if the free radical is located on the bead surface, subsequent polymerization may lead to protrusive and asymmetric beads.¹⁵ The production of asymmetric particles may be evidence for phase separation after polymerization of the monomer, which swells the crosslinked seed particles during the second stage of polymerization. Formation of new particles can be observed by the competition between the beads adsorptive oligomeric free radicals onto the preexisting beads and micellization of oligomeric free radicals in the aqueous medium.

Figures 7–10 show the effect of styrene and KPS contents on bead size and the size distribution in



Figure 8 SEM microphotographs of PS beads at the second stage: (a) series 2, no. 2; (b) series 3, no. 2; and (c) series 4, no. 2.



Figure 9 SEM microphotographs of PS beads at the second stage: (a) series 2, no. 3; (b) series 3, no. 3; and (c) series 4, no. 3.

the second stage as listed in Table I. In Figure 7, from series 2–4 (step 1 in each series in Table I), the concentration of DVB (10 mol %) and KPS (0.25%) was fixed with various amounts of styrene and water to control the solid content to be 15%. In this experimental condition, bead size is slightly increased from 0.92 to 1.19 μ m with styrene content without changing size distribution.

Figure 8 shows SEM photographs of the beads polymerized with various amounts of styrene, 10 mol % DVB, and 0.5% KPS (step 2 in series 2–4 in Table I). For the PS beads with 10 g styrene, bead size is 1.07 μ m, whereas those with 20 g and 30 g styrene are 1.23 μ m and 1.34 μ m, respectively. Thus, bead size increased with monomer content without disturbing size distribution.

Figure 9 shows SEM photographs of the beads prepared by step 3 in series 2-4 in Table I, with various amounts of styrene and fixed 10 mol % DVB and 1% KPS. In this experimental condition, the larger the styrene content, the larger the bead size is obtained as observed in previous experiments, and monodispersity is not significantly varied with styrene content.



Figure 10 SEM microphotographs of PS beads at the second stage: (a) series 2, no. 4; (b) series 3, no. 4; and (c) series 4, no. 4.



Figure 11 SEM microphotographs at series 5 at each stage: (a) at the first stage; (b) at the second stage; and (c) at the third stage.

Figure 10 represents the SEM photographs of the beads polymerized with various amounts of styrene, and fixed amounts of DVB (10 mol %) and KPS (1.5%). The size of the beads with 10 g styrene was 1.13 μ m, whereas those with 20 g and 30 g styrene were 1.36 μ m and 1.51 μ m, respectively. Bead size was enlarged with monomer content without generation of secondary small particles. Styrene (30 g) is the maximum content to induce monodisperse particles without formation of the secondary small particles. If styrene monomer is added, >30 g, the secondary small particles will be observed. This may arise from the critical concentration of monomer that may possibly be absorbed into preexisting particles. On the other hand, it is likely that a surface area of the seeds must exceed critical value to suppress the nucleation of new particles. If seed particle concentration does not exceed this critical value, small particles may be formed in a later stage of reaction, producing polymodal size distribution.^{8,16} The best way to obtain monodisperse large size beads would be by seed polymerization which controls seed latex concentration.

Figure 11 shows the SEM microphotographs of the beads of series 5 at the end of each stage of continuous polymerization. Bead size was 0.8 μ m at the first stage, grown up to 1.6 μ m at the second stage, and then enlarged >2 μ m at the third stage. In addition, the formation of spherical particles indicates the absence of the phase separation between the seed particles and polymers formed at the later stage of the reaction.

Figure 12 shows the size and dispersity of the beads with the reaction time during the third stage. The beads uniformly grow with the reaction time. In the beginning of the continuous process, styrene monomer is not saturated at the aqueous phase before the addition of the initiator. The monomer dissolved in water diffuses into preexisting polymer particles that are stabilized by the sulfate ion, then polymerization continues. Thus, it is considered that the monomer added at the later stage can be converted to oligomeric radicals, which are adsorbed into preexisting polymer particles and enlarge bead size. The suggested mechanism will not generate the small particles in the second or third stage. It is believed that the continuous polymerization at the inner part of the bead surface would induce a formation of spherical particles. On the other hand, phase separation or protrusion by the capture of the free radicals may occur.

CONCLUSIONS

Micron-sized monodisperse crosslinked PS beads have been prepared by a modified multistage emulsion polymerization using styrene monomer, DVB crosslinking agent and KPS initiator in the absence of emulsifier. In addition, the lower the reaction temperature, the larger the bead sizes were obtained. Particle growth of the preexisting polymer seeds using the multistage emulsion polymerization at 60°C was required to obtain the monodisperse



Figure 12 SEM microphotographs of PS beads prepared by seeded polymerization at series 5: (a) 12 h; (b) 13 h; and (c) 14 h.

crosslinked PS beads with their sizes $>2 \mu m$. When the monomer was added up to three times as much as the amount at the first stage, bead size increased and size distribution was monodisperse without a formation of secondary small particles by micellar nucleation. In addition, bead size was increased with initiator and newly added monomer contents at the second stage. The capture mechanism of the free radicals, which are absorbed into growing seed particles at the second or third stage, is similar to that of the previous reports in seed polymerization. As the particle size grows, the number of the free radical in the growing particles increases and conversion of the next stage is continuously increased. It is considered that the continuous absorption of the oligometric radicals into preexisting beads induces the enlargement of spherical monodisperse beads. If the captured free radicals are polymerized at the surface of the bead, it may lead to the formation of asymmetrically shaped particles.

REFERENCES

- 1. Cha, Y. J.; Choe, S. J Appl Polym Sci 1995, 58, 147.
- Zou, D.; Derlich, V.; Gandhi, K.; Park, M.; Sun, L.; Kriz, D.; Lee, Y. D.; Kim, G.; Aklonis, J. J.; Salovey, R. J Polym Sci, Polym Chem Ed 1990, 28, 1909.

- Zou, D.; Ma, S.; Guan, R.; Park, M.; Sun, L.; Aklonis, J. J.; Salovey, R. J Polym Sci, Polym Chem Ed 1992, 30, 137.
- Gandhi, K.; Park, M.; Sun, L.; Zou, D.; Li, C. X.; Lee, Y. D.; Aklonis, J. J.; Salovey, R. J Polym Sci, Polym Phys Ed 1990, 28, 2707.
- Park, M.; Gandhi, K.; Sun, L.; Salovey, R.; Aklonis, J. J. Polym Eng Sci 1990, 30, 1158.
- Ugelstad, J.; Mork, P. C.; Kaggerud, K. H.; Ellingsen, T.; Berge, A. Adv Colloid Interf Sci 1980, 13, 101.
- Grancio, M. R.; Williams, D. J. J Polym Sci, Polym Chem Ed 1970, 8, 2617.
- Chung-li, Y.; Goodwin, J. W.; Ottewill, R. H. Progr Collid Polym Sci 1976, 60, 163.
- Fitch, R. M.; Shin, L. B. Progr Colloid Polym Sci 1975, 56, 1.
- Kao, C. I.; Gundlach, D. P.; Nielsen, R. T. J Polym Sci, Polym Chem Ed 1984, 22, 3499.
- Goodall, A. R.; Wilkinson, M. C.; Hearn, J. J Polym Sci, Polym Chem Ed 1977, 15, 2193.
- 12. Smith, W. V.; Ewart, R. H. J Chem Phys 1948, 16, 592.
- 13. Bovey, F. A.; Kolthoff, I. M. J Polym Sci 1950, 5, 487.
- Vanderhoff, J. W. J Polym Sci, Polym Sym, Ed 1985, 72, 161.
- Sheu, H. R.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci, Polym Chem Ed 1990, 28, 629.
- Hergeth, W. D.; Bittrich, H. J.; Eichorn, F.; Schlenker, S.; Schumutzler, K.; Steinau, U. J. Polymer 1989, 60, 1913.