Highly Crosslinked Micron-Sized, Monodispersed Polystyrene Particles by Batch Dispersion Polymerization, Part 1: Batch, Delayed Addition, and Seeded Batch Processes

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ABSTRACT: The seeded batch dispersion polymerization with or without monomer absorption was compared with the batch polymerization and delayed addition by batch polymerization, to prepare the highly crosslinked, monodispersed polystyrene (PS) particles. The seeded batch polymerization was carried out under the variation of styrene (in second stage)/styrene (in PS seed) (St/St) ratio, divinylbenzene (DVB) concentration, and polymerization temperature using 1.9-μm monodispersed PS seed particles. The experimental results imply that the seeded batch process is more efficient method that could avoid the sensitive particle nucleation step in the presence of the crosslinker than the batch and delayed addition processes. Without monomer absorption, 2.3-μm uniform crosslinked PS particles with 7 wt % of the DVB were prepared in 1/1 (St/St) ratio. In comparison, with the monomer absorption, monodispersed and smooth-surfaced PS particles containing 20 wt % of the DVB were formed. A total of 5% weight loss of the crosslinked PS particles determined by TGA occurred from 353.8 to 374.8°C, and the degree of swellability in toluene decreased from 150 to 104.5% with increasing the DVB concentration from 5 to 20 wt % because of the increase of the crosslink density of the particles. The seeded polymerization, especially through monomer absorption procedure, is a novel way to obtain highly crosslinked, monodispersed PS particles. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 297–307, 2010

Key words: seeded batch process; highly crosslinked micron-sized PS particles; divinylbenzene; TGA; swellability

INTRODUCTION

Monodispersed polymeric microspheres are used in a wide variety of scientific and technological applications with high value-added materials, such as column packing material,[1] toners,[2] biomedical applications,[3] and catalyst supports.[4,5] Primarily, there have been strong demands[6–9] for highly crosslinked polymer beads with superior heat resistance, solvent resistance, and mechanical strength to serve as a spacer for display panel, ion exchangers, polymer-supported catalysis, conductive ball, etc.

Micron-sized uniform particles can be made by the successive seeded emulsion polymerization[10] or the activated swelling and suspension polymerization methods.[11] However, these processes are complex, time-consuming, and difficult to implement on a large scale.

The recent technique in making monodisperse beads with micrometer diameter is a dispersion polymerization.[12–16,17] This process is very attractive for large-scale preparation of such particles. However, there are many citations[15,16,18–25] in the literature to attest to the fact that dispersion polymerization failed when crosslinking agents are present. One often finds flocculation or coagulation of the product along with odd-shape particle and a broad size distribution. Tseng and et al.[15] described about the dispersion polymerization of styrene (St) with small amount of divinylbenzene (DVB), in which the particle size changed and the size distribution was significantly broadened for the addition of 0.3 wt %, and with further increase in DVB concentration, coagulation was observed. Shen et al.[16] also reported that 0.3 wt % ethylene glycol dimethacrylate (EGDMA) gave partial flocculation of the PMMA dispersion and the total flocculation was observed at 0.6 wt %. Recently, some studies[18-25] on how to overcome flocculation and deformation in dispersion polymerization in the presence of crosslinker have been reported. Generally, the crosslinking agents interfere with the sensitive particle nucleation step causing flocculation and

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TABLE I
Preparation of PS Seed

Ingredients	Wt (%)	Amount (g)
St	12.58	15
EtOH	86.04	102.6
PVP K-30	1.25	1.5
AIBN	0.13	0.15
Total	100	119.25

Polymerization condition: 70°C, 100 cycles/min for 24 h.

deformation.[15,16,18,19] Song and Winnik[20] reported that when DVB or EGDMA was added at the end of the nucleation stage, monodispersed particles could be obtained. Also, some researchers tried to overcome the problem because of the presence of crosslinker by long time addition method.[20-23]

In this work, various polymerization processes such as batch, delayed addition, and seeded batch processes with or without monomer absorption were compared to prepare highly crosslinked monodispersed polystyrene (PS) particles under the various polymerization conditions. Primarily, this study focuses on the seeded batch dispersion polymerization using the monodispersed PS seed to investigate the polymerization factors, such as St (in second stage)/St (in PS seed) ratio, DVB concentration, and polymerization temperature. Part II will also be reported in succession on the preparation of the highly crosslinked PS particles by semicontinuous and seeded semicontinuous processes.

EXPERIMENTAL

Materials

Styrene (Junsei) was washed with 10 wt % aqueous NaOH solution to remove hydroquinone (HQ). Divinylbenzene (55%, a mixture of isomers, Aldrich) was passed through an activated aluminum oxide column to remove inhibitor and stored at −10°C before use. 2.2′-Azobis(isobutyronitrile) (AIBN, Junsei) was recrystallized from methanol. All other materials were used without further purification. Ethanol (EtOH, Daejung chemical) and distilled deionized water were used as a polymerization medium. Poly(N-vinyl pyrolidone) (PVP K-30, Junsei) was used as steric stabilizer.

Dispersion polymerization

Batch process

The dispersion polymerization of styrene by batch process was carried out under the reaction conditions as shown in Table I with the DVB concentrations from 0.1 to 1 wt % (based on monomer).
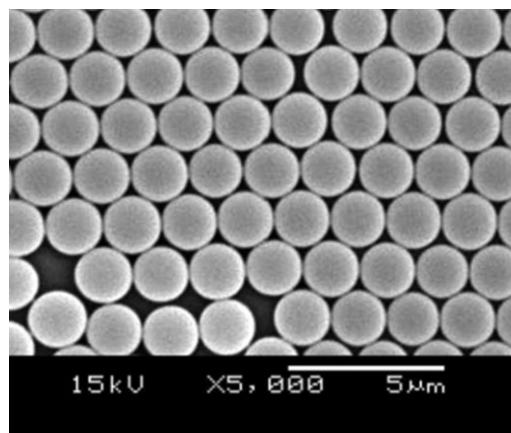
Figure 1 Scanning electron micrograph of PS seed particles.

Delayed addition by batch process

In this study, the delayed addition process in which the DVB adds after the nucleation period was used. The polymerization condition and procedure are similar to those described in Table I, except that the DVB (0.35–1 wt %) adds 1, 3, 6, 12, and 24 h after the start of the polymerization, respectively.

Seeded batch process

Preparation of PS seed. Figure 1 shows the SEM micrograph of the PS seed particles prepared by the polymerization method as shown in Table I. The PS seed latex particles were all uniform in 1.9-μm diameter, and the polymerization showed higher than 96 wt % conversion determined by gravimetry with a negligible coagulum.

Seeded batch process. Table II shows the standard for the preparation of crosslinked PS particles by seeded batch dispersion polymerization. The St/St ratio indicates the ratio between amount of styrene monomer used in second and first stages (PS seed preparation), which was divided into 1/1 and 0/1 in

TABLE II
Standard Recipe for Seeded Batch Process
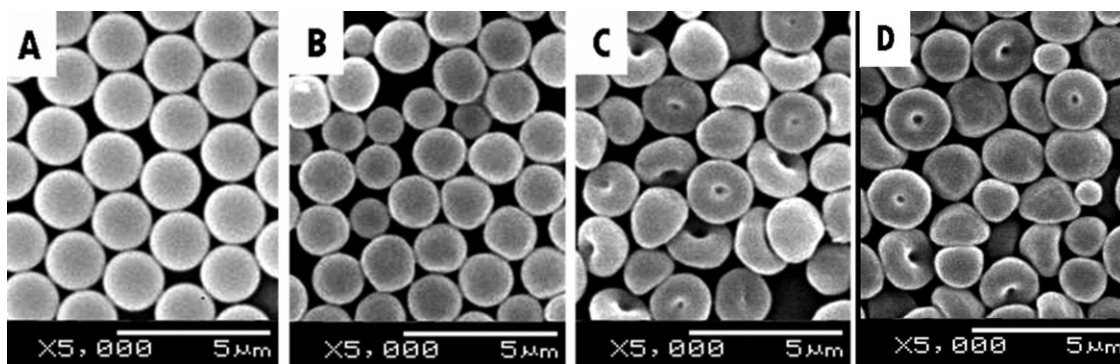**(Amounts in grams)**

Ingredients	First stage	Second stage	
	PS seed[a]	1/1[b]	0/1[b]
St	0.46	0.46	0
EtOH	3.1	3.1	3.1
PVP K-30	0.046	–	–
DVB[c]	–	0–0.92	0–0.46
AIBN	0.0046	0.0046	0.0046

Polymerization condition: 70°C, 100 cycles/min for 24 h.
[a] PS seed latex prepared in Table I.
[b] Styrene (in second stage)/styrene (in PS seed) ratio.
[c] 0–100 wt % of DVB based on total amount of St monomer used in first and second stages.

Figure 2 Scanning electron micrographs of the PS particles prepared with four different DVB concentrations [(A) 0 wt %, (B) 0.1 wt %, (C) 0.35 wt %, and (D) 1 wt % of DVB].

this study. The DVB concentration used in this experiment was in the range of 0–100 wt % based on total amount of styrene used in first and second stages. Polymerization was carried out in a shaking water bath with an agitation speed of 100 cycles/min at 70°C for 24 h.

Seeded batch process with monomer absorption. In this study, the monomer absorption procedure for the PS seed particles prior to the seeded polymerization was carried out to compare with those of nonabsorption process. The determination of the optimum condition for monomer absorption was also examined in a shaker operating at 100 cycles/min and at 25°C for 30 min–48 h.

Characterization

Morphology of the polymer particles and their characteristics such as particle size and size distribution were analyzed using a scanning electron microscopy (SEM, Jeol JSM-6380LV) and optical microscopy (OM, Leica DMLM). The sample was prepared by taking one drop of the final dispersion diluted in about 2–3 mL of EtOH, and one drop of the diluted dispersion was coated on the aluminum stud and dried at room temperature for 24 h. Then sample was sputter-coated with gold and examine at 15 kV. The particle size of the latexes was measured with photographs, and the particle size distribution (PSD) was also determined as the ratio of the number ($\overline{D_n}$) and weight ($\overline{D_w}$) average diameters as follows[17]:

$$\overline{D_n} = \frac{\sum\limits_{1=0}^{N} D_i}{N} \tag{1}$$

$$\overline{D_W} = \frac{\sum\limits_{1=0}^{N} D_i^4}{\sum\limits_{1=0}^{N} D_i^3}, \tag{2}$$

where N is the total number of particles counted and D_i is the diameter of particle.

$$\text{PSD} = \frac{\overline{D_W}}{\overline{D_n}} \tag{3}$$

The percent conversion of the dispersion polymerization was determined by gravimetric method after drying at 60°C for 24 h. The thermal stability of PS microspheres was estimated as the temperature of the occurrence of 5 wt % loss using a TGA Q-50 from TA instruments with a heating rate of 10°C/min in the temperature range from 25 to 700°C. All measurements were made under an N_2 gas flow rate of 50 mL/min.

For the determination of swellability of the PS microspheres, 0.5 g of crosslinked PS particles was put into 5 mL of toluene at room temperature and then observed the change in the size and shape using an OM (Leica DMLM) with time. The swellability of the particle was calculated as follows[22]:

$$\text{Swellability}(\%) = \frac{\overline{D_1}}{\overline{D_0}} \times 100,$$

where $\overline{D_0}$ is the number-average diameter of the dried, original particle, $\overline{D_1}$ is the number-average diameter at the maximum swelling point observed after 48 h. The $\overline{D_n}$ kept basically unchanged after 12 h.

RESULTS AND DISCUSSION

Batch process

The effect of DVB concentration in dispersion polymerization of styrene by batch process was investigated. Figure 2 shows the SEM micrographs of the PS particles prepared with three different DVB concentrations (0.1–0.35 wt %) according to the polymerization as shown in Table I. In the absence of

TABLE III
Dispersion Polymerization by Delayed Addition Process

	DVB (wt %)[a]	Addition point of DVB (h)[b]	$\overline{D_n}$ (μm)	PSD	Particle morphology
A	0.35	15 min	–		Doughnut-like particles
B	0.35	1	–		
C	0.35	3	1.9	1.086	Smooth-surfaced particles and generation of secondary particles
D	0.35	6	1.9	1.001	Monodispersed and smooth-surfaced particles
E	0.5	3	–		Deformed particles on the surface
F	0.5	12	–		Raisin-like particles
G	1	6	–		Coagulation
H	1	12	–		Raisin-like particles and generation of secondary particles
I	1	24	–		Raisin-like particles and generation of secondary particles

Polymerization condition: 70°C, 100 cycles/min for 25–48 h.
[a] wt % of DVB based on St monomer.
[b] The addition point of DVB after the beginning of the reaction.

DVB, 1.9-μm monodispersed PS particles were prepared [Fig. 2(A)]. In comparison, the polydisperse and nonspherical-shaped PS particles were obtained [Fig. 2(B)] when 0.1 wt % of DVB was present in the initial charge. The doughnut-like severely deformed particles were also observed at 0.35 wt % due to the phase separation resulting from localized crosslink density [Fig. 2(C)], and deformation and flocculation of particles were obtained at 1 wt % [Fig. 2(D)].

In general, dispersion polymerization is very sensitive to the changes of reaction parameters, and these changes influence the particle size, size distribution, and morphology.[12,14,15] This phenomenon is likely to occur extremely in the presence of DVB.[15,19,20] Furthermore, DVB is more reactive than styrene ($r_{St}/r_{m\text{-}DVB}$ = 0.6/0.88, $r_{St}/r_{p\text{-}DVB}$ = 0.15/1.00) in the copolymerization of St/DVB,[20,21] resulting in the particle nucleation of crosslinked structure at the initial stage of the polymerization. The crosslinked particle nuclei grow up odd-shaped particles in the end with secondary particle nucleation as shown in Figure 2(C,D). Therefore, the more novel technique that could overcome the sensitive particle nucleation stage in the presence of the crosslinker should be developed.
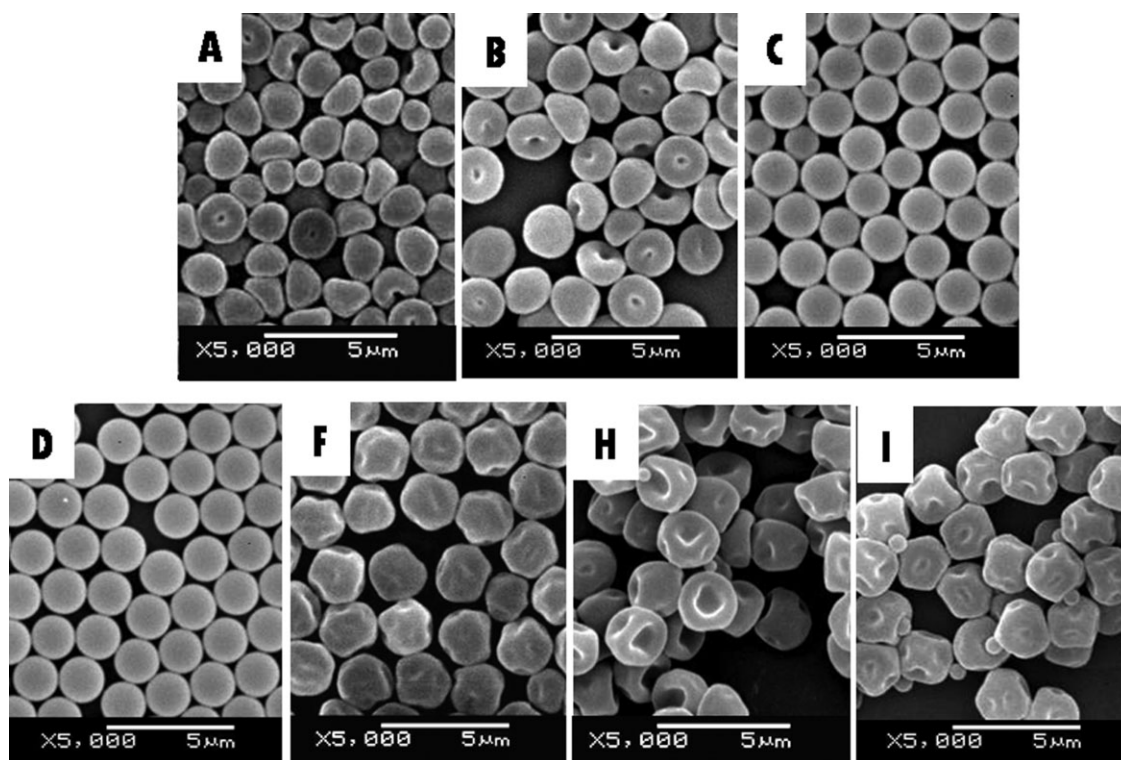
Delayed addition by batch process

Table III represents the particle size and particle morphology of the PS particles prepared with five different addition times in the range of 0.35–1 wt % of the DVB by delayed addition process.

Figure 3 shows the particle size, particle morphology, and SEM micrographs of the PS particles prepared with three different DVB concentrations (0.35, 0.5, and 1 wt % DVB) depending on the variation of addition time ranging from 0 to 24 h after the start of the reaction as shown in Table III. Doughnut-like

particles were prepared on adding 0.35 wt % DVB at the beginning of the reaction (0 min) [Fig. 2(C)], and the same shaped particles were also observed on adding the DVB after 15 min [Fig. 3(A), conversion: 9.7%] and 1 h [Fig. 3(B), conversion: 15.6%]. On adding the DVB after 3 h (conversion: 32%), not only monodispersed and smooth-surfaced main particles but also small amount of secondary particles were observed together [Fig. 3(C)]. When 0.35 wt % DVB was added after 6 h (conversion: 70%), monodispersed and smooth-surfaced PS particles were prepared [Fig. 3(D)]. Particle deformation was also observed on adding 0.5 wt % DVB after 3 h and even after 12 h [Fig. 3(F), conversion: 84%]. In cases of adding 1 wt % DVB after 12 [Fig. 3(H)] and 24 h (conversion: 92%), deformation and flocculation of particles were occurred with the nucleation of small-sized secondary particles [Fig. 3(I)].

The delayed addition process in which the crosslinker adds after the particle nucleation is likely to be a more effective way in preparing crosslinked monodispersed PS particles [Fig. 3(D)] for smaller than 0.35 wt % of DVB compared with the batch process. However, the results shown in Table III and Figure 3 indicate that most of the polymerizations with more than 0.5 wt % of DVB showed severe deformation of the resultant particles along with secondary nucleation. It is known that particle nucleation in the dispersion polymerization of styrene occurs in about 5–6 min after the start of polymerization. This corresponds to a conversion of 15–16%.[26] However, the results obtained by the delayed addition do not follow the 15–16% as shown in Table III. Combining all the results, the delay addition method could not identify the exact addition point in this study. More detailed studies on this subject should be done in the future primarily in the relationships among the effects of

Figure 3 Scanning electron micrographs of the PS particles prepared with different addition points of DVB by delayed addition process [(A) 15 min (B) 1 h (C) 3 h (D) 6 h at 0.35 wt % DVB, (F) 12 h at 0.5 wt % DVB, (H) 12 h, and (I) 24 h at 1 wt % DVB].

particle nucleation, concentration, and addition point of crosslinker, etc. Accordingly, in this study, monodispersed PS seed particles were first prepared by dispersion polymerization to avoid the problem occurring in the particle nucleation from the influence of crosslinker, and then seeded batch polymerization under various reactions was performed as follows.

Seeded batch process

Highly crosslinked monodispersed PS particles were synthesized by the seeded batch dispersion polymerization using the 1.9-μm PS seed particles under the variation of St (in second stage)/St (in PS seed) ratio, DVB concentration, and polymerization temperature. The polymerizations performed in the experiments were all more than 95 wt % conversion.

Effect of St (in second stage)/St (in PS seed) (St/St) ratio

Table IV and Figure 4 show the particle size, size distribution, and particle morphology of the PS particles prepared with five different St (in second stage)/St (in PS seed) ratio in the range of 5–10 wt % of DVB.

In case of St/St ratio of 0/1, 1.9-μm smooth-surfaced uniform PS particles with 7 wt % of DVB

were prepared [Fig. 4(A)], whereas the wrinkly particles for 10 wt % of the DVB were observed [Fig. 4(B)]. However, DVB concentration required to the formation of monodispersed crosslinked PS particles decreased from 7 to 5 wt % [Fig. 4(A,B,C,E,F)] with increasing in the St/St ratio from 0/1 to 1/1. Furthermore, coagulum with many secondary particles was found in case of 1.5/1, at 5 wt % of DVB [Table IV(G)]. The amount of monomer used in the second stage increases considerably with increasing St/St ratio from 0/1 to 1.5/1. For example, the amount of monomer added in the second stage increases from 0.032 to 0.77 g for 0/1 and 1.5/1, respectively, at 7 wt % of DVB. Generally, the polymerizations of 0/1 in the range of 0–10 wt % DVB are likely to occur after enough infiltration of DVB into the PS seed particles, resulting in monodispersed PS particles. In comparison, with the increase in St/St ratio from 0/1 to 1.5/1, the excess amount of monomers including DVB present in the polymerization, resulting in the generation of new crop of small particles with the polymerizations within PS seed particles. In addition, the amount of DVB added at the second stage also increased with the increase in St/St ratio from 0/1 to 1.5/1. Therefore, DVB concentration required in the formation of monodispersed crosslinked PS particles showed the tendency to decrease.

TABLE IV
Effect of St (in Second Stage)/St (in PS Seed) Ratio

	St/St ratio[a]	DVB (wt %)[b]	$\overline{D_n}$ (μm)	PSD	Particle Morphology
A	0/1	7	1.9	1.002	Monodispersed and smooth-surfaced particles
B	0/1	10	2.1	1.004	Wrinkly particles on the surface
C	0.33/1	5	2.1	1.002	Monodispersed and smooth-surfaced particles
D	0.33/1	6	–		Smooth-surfaced and secondary particles
E	0.5/1	5	2.2	1.002	Monodispersed and smooth-surfaced particles
F	1/1	5	2.3	1.001	Monodispersed and smooth-surfaced particles
G	1.5/1	5	–		Generation of secondary particles and coagulation

Polymerization condition: 70°C, 100 cycles/min for 24 h.
[a] St (in second stage)/St (in PS seed) ratio.
[b] wt % of DVB based on total amount of St monomer used in first and second stages.

Effect of DVB concentration

Table V lists the particle size, size distribution, and particle morphology of the PS particles prepared at DVB concentrations from 5 to 70% under the St (in second stage)/St (in PS seed) ratio of 1/1 and 0/1. Figure 5 also shows the SEM micrographs of the crosslinked PS microspheres prepared depending on the different DVB concentrations by the seeded batch dispersion polymerization.

In case of 1/1 in St/St ratio, 2.3-μm smooth-surfaced uniform PS particles with 5 wt % of the DVB were obtained [Fig. 5(A)]; however, small secondary particles were nucleated in the range of 6–10 wt % of DVB [Fig. 5(B)]. The polymerizations with higher than 25 wt % of DVB resulted in the formation of coagulum with generation of secondary particles [Fig. 5(C)].

In case of 0/1 in St/St ratio, monodispersed and smooth-surfaced PS particles with 7 wt % of the DVB were obtained [Fig. 5(D)]; however, uniform particles with wrinkly surface were observed in the range of 10–30 wt % of DVB [Fig. 5(E)]. Further increase to 35–70 wt % of DVB generated deformed particles with submicron-sized secondary particles [Fig. 5(F)]. This results imply that the seeded batch process is a more efficient way in obtaining highly crosslinked monodispersed PS particles with 5–7 wt % of DVB than batch and delayed addition processes described earlier. In other words, the two-stage batch dispersion polymerization with already made monodispersed PS seed particles is one of the novel methods that could avoid the sensitive particle nucleation step in the presence of the crosslinking agent and lead to highly crosslinked monodispersed polymer particles than the conventional batch process.
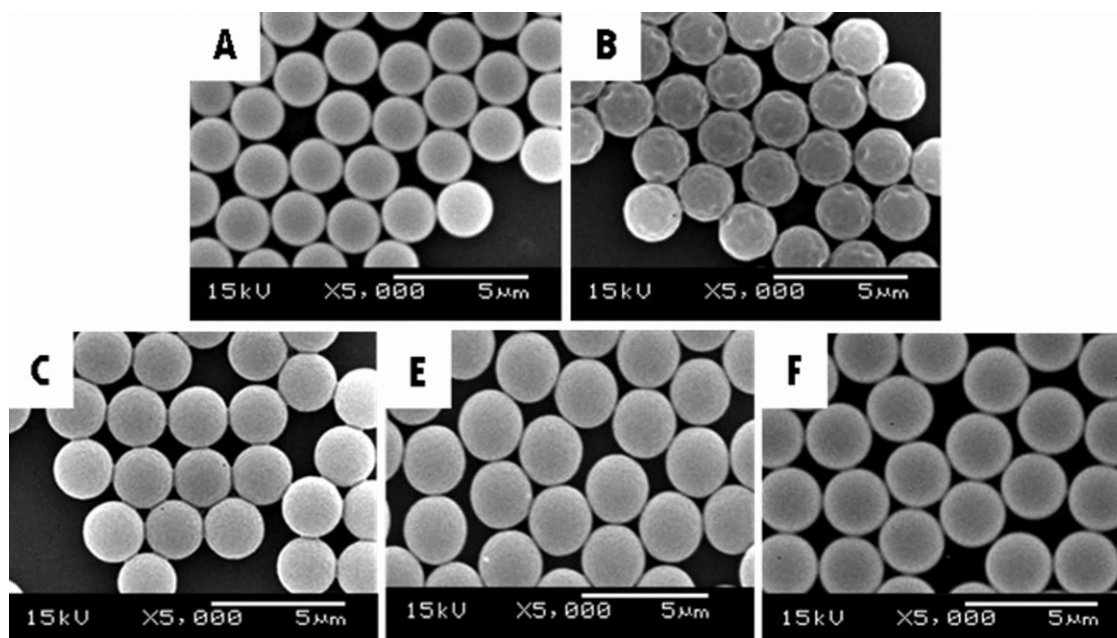
Figure 4 Scanning electron micrographs of crosslinked PS particles prepared with different St/St ratio by seeded batch dispersion polymerization [(A) 7 wt % (B) 10 wt % DVB at 0/1, (C) 5 wt % DVB at 0.33/1, (E) 5 wt % DVB at 0.5/1, and (F) 5 wt % DVB at 1/1 in St/St ratio].

TABLE V
Effect of DVB Concentration

	St/St ratio[a]	DVB (wt %)[b]	$\overline{D_n}$ (µm)	PSD	Particle morphology
A	1/1	5	2.3	1.001	Monodispersed and smooth-surfaced particles
B	1/1	6–10	–		Smooth-surfaced particles and generation of secondary particles
C	1/1	25	–		Generation of secondary particles and coagulation
D	0/1	7	2.1	1.001	Monodispersed and smooth-surfaced particles
E	0/1	10–30	2.2–2.5	1.003	Monodispersed and wrinkly particles
F	0/1	35–70	–		Deformed and generation of secondary particles

Polymerization condition: 70°C, 100 cycle/min for 24 h.
[a] St (in second stage)/St (in PS seed) ratio.
[b] wt % of DVB based on total amount of St monomer used in first and second stages.

Effect of polymerization temperature

Table VI and Figure 6 show the effect of the polymerization temperature ranging from 55 to 80°C on the particle size, size distribution, and particle morphology of the PS particles prepared under various DVB concentrations in St/St ratio of 1/1 and 0/1. It was found that the conversion of the latices polymerized at more than 55°C reaches up to 95% in conversion, whereas the conversion reaches around 60–70% at 50°C. In comparison, most of the latices prepared at 75 and 80°C also showed deformed main particles with secondary nucleated small particles.

In case of 1/1 in St/St ratio, monodispersed PS particles were effectively prepared at 6–7 wt % of the DVB concentration by reducing the polymerization temperature to 55–65°C [Fig. 6(A–C)], whereas secondary particles were observed with 7 wt % of DVB at 70–80°C [Fig. 6(D)]. With a further increase to 10 wt % of the DVB, the submicron-sized secondary particles were also observed at 55–60°C [Fig. 6(E)].

In case of 0/1 in St/St ratio, monodispersed and smooth-surfaced PS particles containing 20 wt % of DVB were prepared at 60°C as the polymerization temperature [Fig. 6(G)], whereas wrinkly particles on the surface formed at 70°C for 7 wt % DVB [Fig. 6(F)]. In addition, dimple particles with secondary nucleated small particles were also observed at 70–80°C in the range of 25–35 wt % DVB [Fig. 6(I)], and at 60°C and 40 wt % of DVB concentration [Fig. 6(K)].

The amount of monomer used at the second stage in 0/1 of St/St ratio is very small (about 1/16 based on 7 wt % DVB) compared with that of 1/1 (St/St) ratio, which is only DVB itself. The
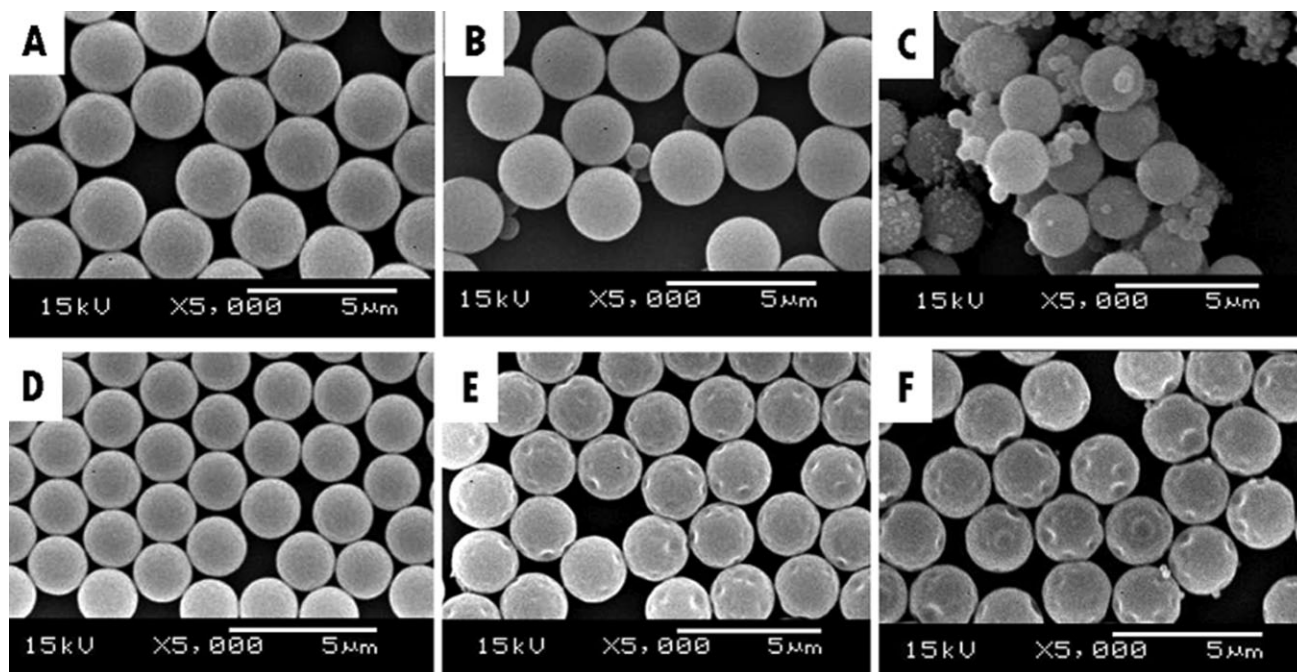

Figure 5 Scanning electron micrographs of the PS particles prepared at different DVB concentrations by seeded batch dispersion polymerization [(A) 5 wt % (B) 7 wt % (C) 25 wt % DVB at 1/1, (D) 7 wt % (E) 30 wt % (F) 50 wt % DVB at 0/1 in St/St ratio].

TABLE VI
Effect of Polymerization Temperature

|	St/St ratio[a]	DVB (wt %)[b]	Pol^n Temp (°C)	$\overline{D_n}$ (µm)	PSD	Particle morphology
A	1/1	6	55, 60	2.4	1.001	Monodispersed and smooth-surfaced particles
B	1/1	7	55, 60	2.4	1.002	Monodispersed and smooth-surfaced particles
C	1/1		65	2.45	1.003	Monodispersed and smooth-surfaced particles
D	1/1		70, 75, 80	–		Smooth-surfaced and secondary particles
E	1/1	10	55, 60	–		Smooth-surfaced and secondary particles
F	0/1	7	70	2.4	1.004	Wrinkly particles on the surface and narrow size distribution
G	0/1	20	60	2.4	1.003	Monodispersed and smooth-surfaced particles
H	0/1		65, 70	2.5	1.003	Wrinkly particles on the surface
I	0/1	25–35	70, 75, 80	–		Dimple particles and generation of secondary particles
J	0/1	35	60	2.5	1.004	Wrinkly particles on the surface
K	0/1	40	60	–		Wrinkly particles and generation of secondary particles

Polymerization condition: 70°C, 100 cycles/min for 24 h.
[a] St (in second stage)/St (in PS seed) ratio.
[b] wt % of DVB based on total amount of St monomer used in first and second stages.

reactivity of DVB in the copolymerization of styrene with DVB in general increases with the polymerization temperature and vice versa. The crosslinking reaction on the surface of the PS seed particles would therefore increase with reaction temperature, resulting in the formation of deformed main particles with secondary nucleated small particles. However, the crosslinking reaction becomes sluggish with decreasing the reaction temperature, the monomer added in the second stage is easily swollen into the PS seed particles before the polymerization, and the polymerization would lead to monodispersed PS particles. That is the reason why highly crosslinked monodispersed PS
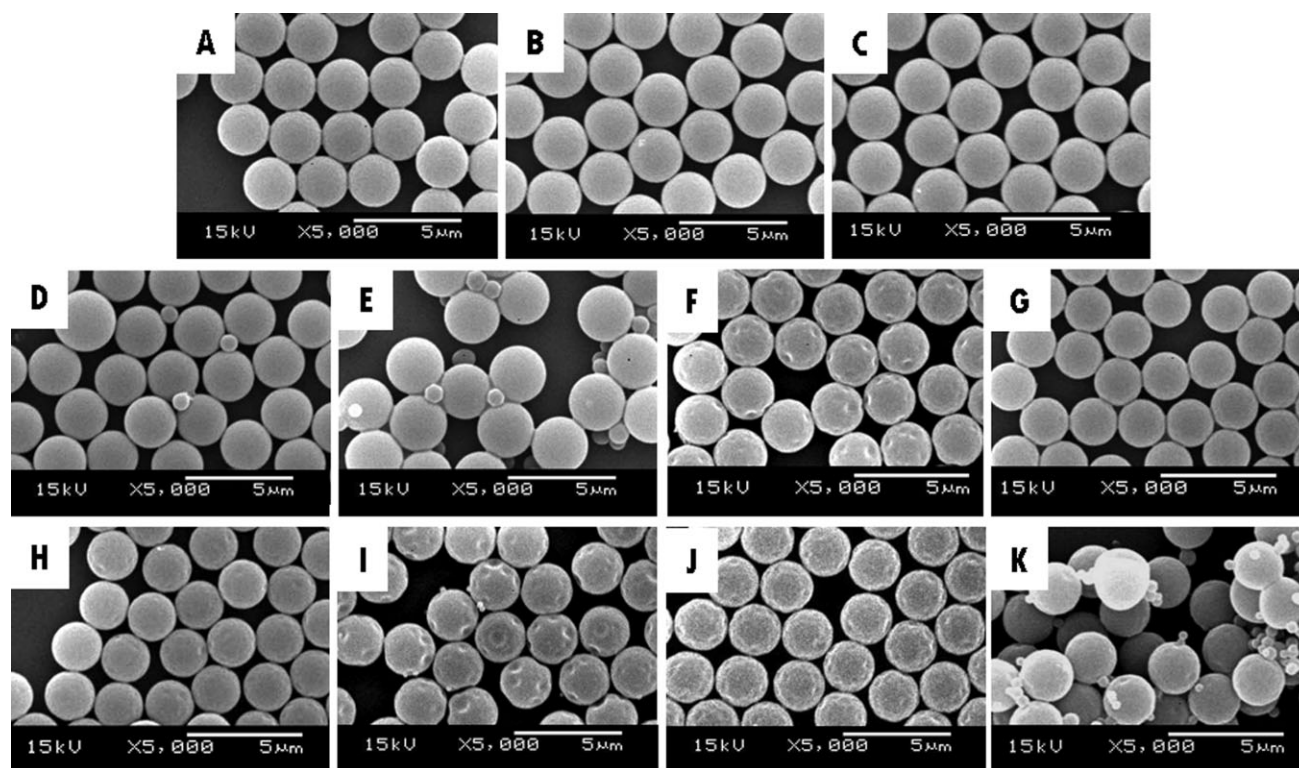
Figure 6 Scanning electron micrographs of crosslinked PS particles prepared at different polymerization temperatures by seeded batch dispersion polymerization [(A) 6 wt % (B) 7 wt % at 60°C (C) 7 wt % at 65°C (D) 7 wt % at 80°C (E) 10 wt % at 55°C in St/St = 1/1, (F) 7 wt % at 70°C (G) 20 wt % at 60°C (H) 20 wt % at 65°C (I) 35 wt % at 80°C (J) 35 wt % (K) 40 wt % at 60°C in St/St = 0/1].

TABLE VII
Seeded Batch Process with Monomer Absorption

	St/St ratio[a]	DVB (wt %)[b]	Pol^n temp (°C)	$\overline{D_n}$ (µm)	PSD	Particle morphology
A	1/1	10, 20	70	2.3	1.003	Monodispersed and smooth-surfaced particles
B	1/1	25	60, 70	–		Generation of secondary particles and coagulation
C	0/1	7	70	2.0	1.002	Monodispersed and smooth-surfaced particles
D	0/1	10		2.0	1.004	Dimpled particles on the surface and narrow size distribution
E	0/1	20		2.3	1.004	Dimpled particles on the surface and narrow size distribution
F	0/1		60	2.3	1.004	Monodispersed and smooth-surfaced particles
G	0/1	25, 35		2.45	1.003	Dimpled particles on the surface and narrow size distribution
H	0/1	50	60	2.5	1.004	Dimpled particles on the surface and generation of secondary particles
I	0/1	50	70	2.5	1.004	Dimpled particles on the surface and generation of secondary particles

Polymerization condition: 70°C, 100 cycles/min for 24 h.
[a] St (in second stage)/St (in PS seed) ratio.
[b] wt % of DVB based on total amount of St monomer used in first and second stages.

particles containing 20 wt % DVB were prepared in the reaction conditions at 60°C and 0/1 in St/St ratio compared with that of 7 wt % of DVB at 70°C and 1/1 in St/St ratio, because of a facile infiltration of DVB crosslinker within the particles by reducing the reaction temperature at 60°C.

Seeded batch process with monomer absorption

The seeded batch polymerization was also carried out after the monomer absorption process at 25°C, 100 cycles/min for 1 h to compare with those by nonabsorption process in making highly crosslinked monodispersed PS particles. The monomer absorption for 1 h was found to be the optimum condition in which monodispersed and smooth-surfaced crosslinked PS particles were made without any formation of twin- or triplet-shaped particles.

Table VII and Figure 7 show the particle size, size distribution, and particle morphology of the crosslinked PS particles prepared under the variation of DVB concentration, polymerization temperature, and St (in second stage)/St (in PS seed) ratio through the monomer absorption procedure.

For the St/St ratio of 1/1, monodispersed and smooth-surfaced PS particles containing 20 wt % DVB were prepared at polymerization temperature range from 60 to 70°C [Fig. 7(A)], whereas coagulum with many secondary particles was found for 25 wt % of DVB [Fig. 7(B)]. On the other hand, without
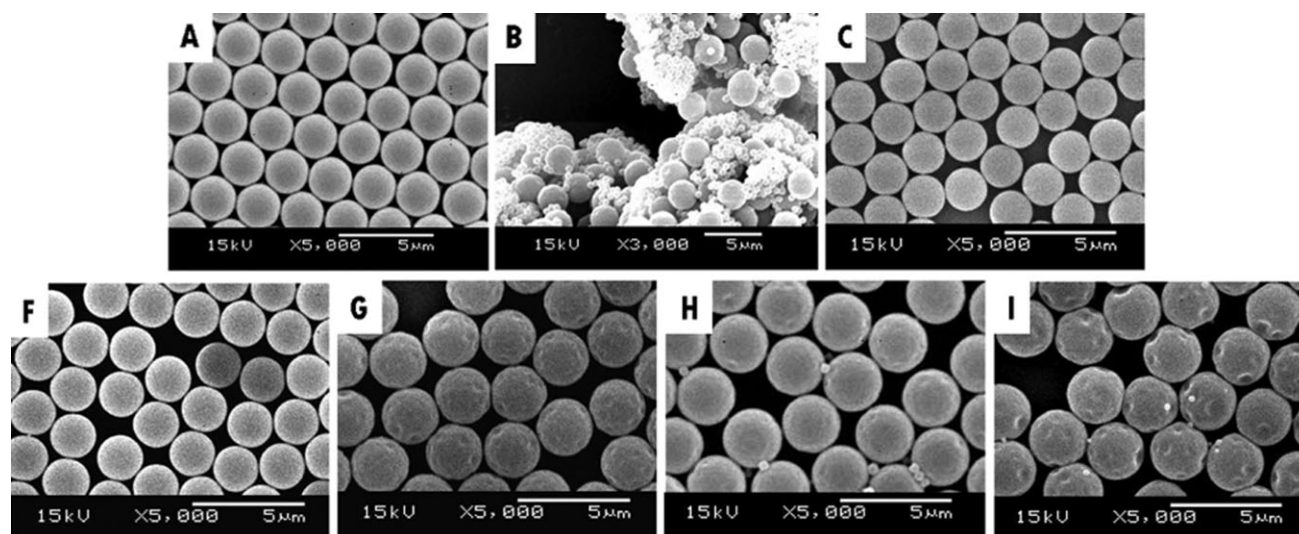
Figure 7 SEM photographs of crosslinked PS particles prepared with monomer absorption [(A) 20 wt % (B) 25 wt % at 70°C in St/St = 1/1, (C) 7 wt % (F) 20 wt % at 70°C (G) 35 wt % (H) 50 wt % at 60°C (I) 50 wt % at 70°C in St/St = 0/1].
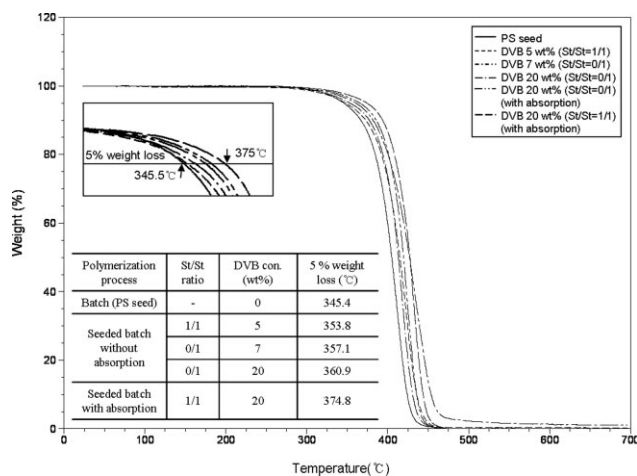
Figure 8 The thermogravimetry curves of crosslinked PS particles with different DVB concentrations from 0 to 20 wt %.

monomer absorption process, uniform crosslinked PS particles could be made only for 5–7 wt % of DVB at 60°C [Figs. 5(A) and 6(B)] and secondary nucleated small particles were found for 7 wt % DVB at 70°C [Fig. 6(C)]. The result shows that in adopting the monomer absorption procedure, the sufficient infiltration of monomer into the PS seed particles before the polymerization and a facile polymerization inside the particles occurred at DVB concentration as high as 20 wt %.

In case of 0/1 in St/St ratio, monodispersed and smooth-surfaced PS particles containing 20 wt % of the DVB were also obtained by reducing the polymerization temperature to 60°C [Fig. 7(F)], and uniform crosslinked PS particles with 7 wt % of DVB were also prepared at 70°C [Fig. 7(C)]. Dimpled particles with narrow size distribution were observed in the range of 25–35 wt % of DVB [Fig. 7(G)]. Further increase to 50 wt % of DVB at 60–70°C dimpled particles on the surface with secondary particles were made [Fig. 7(H,I)]. It is very interesting to note that

these results are very similar to those obtained without monomer absorption as shown in Table VI. That is probably due to the relatively small amount of DVB added at second stage in 0/1, and its facile infiltration into the PS seed particles irrespective of monomer absorption.

Characterization

Thermal stability

Figure 8 shows the TGA thermogram of crosslinked PS particles prepared with four different DVB concentrations ranging from 0 to 20 wt %. No obvious weight loss was observed in temperature ranges between 50 and 300°C for all samples, and the 5% weight loss of PS seed particles was observed at 345.4°C. In comparison, 5% weight loss of the crosslinked PS particles prepared by the seeded batch process without monomer absorption was occurred from 353.8 to 360.9°C with increasing DVB concentration from 0 to 20 wt %, and monodispersed crosslinked PS particles containing 20 wt % of DVB through monomer absorption showed the highest 5% weight loss temperature at 374.8°C. It can be seen that the thermal stability of the crosslinked PS particles increased obviously with increasing DVB concentration, implying the increase of crosslinked density inside the particles.

Swelling test

Table VIII shows the swellability of monodispersed crosslinked PS particles determined in toluene. The swellability of the crosslinked PS particles in general decreased with increasing concentration of DVB as expected. PS seed particles without the DVB were dissolved easily in toluene [Table VIII(A)]. The crosslinked PS particles with 5 wt % DVB prepared at 1/1 in St/St ratio and 70°C showed the highest swellability, 150.0% [Table VIII(B)] and PS particles with 7 wt % DVB formed at 60°C also showed 133.3% [Table VIII(C)]. The swellability of the

TABLE VIII
Swellability of Crosslinked PS Particles

	Polymerization process	St/St ratio[a]	Temp (°C)	DVB con. (wt %)[b]	Swellability[c] (%)
A	Batch (PS seed)	−	70	0	Soluble
B	Seeded batch without absorption	1/1	70	5	150.0
C	Seeded batch without absorption	1/1	60	7	133.3
D	Seeded batch without absorption	0/1	70	7	127.6
E	Seeded batch without absorption	0/1	60	20	108.3
F	Seeded batch with absorption	1/1	70	20	104.5
G	Seeded batch with absorption	0/1	60	20	106.0

[a] St (in second stage)/St (in PS seed) ratio.
[b] Based on total amount of St monomer used in first and second stages.
[c] Determined in toluene.

crosslinked PS particles prepared at 0/1 in St/St ratio decreased from 127.6 to 108.3% with the increase of DVB concentrations from 7 to 20 wt % [Table VIII (D), (E)]. Especially, monodispersed crosslinked PS particle containing 20 wt % of DVB with monomer absorption procedure showed the lowest swellability, 104.5% [Table VIII(F)].

These results indicate that with the increasing of DVB concentrations, the crosslink density distributed in the PS particles increased, leading to the crosslinked particles having good solvent resistance. Especially, monodispersed crosslinked PS particles with 20 wt % DVB (St/St = 1/1) through the monomer absorption procedure were observed the lowest swellability, alluding monomer absorption procedure prior to polymerization is an efficient way in formation of highly crosslinked network of the resultant PS particles.

CONCLUSIONS

Various polymerization processes such as batch, delayed addition, and seeded batch processes with or without monomer absorption were compared to prepare highly crosslinked monodispersed PS particles. In the batch process, nonspherical and doughnut-shaped particles were observed for 0.35 wt % DVB. On the other hand, the delayed addition process was a more effective way to prepare crosslinked monodispersed PS particles for smaller concentration of DVB than 0.35 wt %, in which DVB added 6 h after the beginning of the reaction. In the seeded processes, 1.9-μm PS seed particles were first prepared by dispersion polymerization to avoid the problem occurring in the particle nucleation from the influence of crosslinker, and then seeded polymerizations were performed at various DVB concentration, polymerization temperature, and St (in second stage)/St (in PS seed) ratio at the second stage. For the 1/1 (St/St) ratio, monodispersed and smooth-surfaced PS particles with 7 wt % DVB were prepared under polymerization temperature ranging from 60 to 70°C. Also, with the monomer absorption process, uniformly crosslinked PS particles with 20 wt % DVB were prepared at 70°C. This study also showed that the thermal stability (5% weight loss) and solvent resistance (in Toluene) increased with DVB concentration from 5 to 20 wt %, ranging in 353.8–374.8°C and 150–104.5%, respectively. These results confirm that the seeded polymerization, especially through monomer absorption procedure, is a more efficient way to obtain highly crosslinked, monodispersed PS particles than batch and delayed addition processes.

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