

Highly Crosslinked Micron-Sized, Monodispersed Polystyrene Particles by Semicontinuous Dispersion Polymerization. II. Semicontinuous, Delayed Addition and Seeded Semicontinuous Processes

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ABSTRACT: A highly crosslinked, monodispersed polystyrene (PS) particle was prepared by the seeded semicontinuous dispersion polymerization using ready-made monodispersed PS seed particles. The effects of Styrene (in 2nd stage)/Styrene (in PS seed) ratio, addition point and feeding time of divinylbenzene (DVB), concentration of DVB and polymerization temperature on the particle size, size distribution and morphology of the resulting particles were investigated. Monodispersed PS particles with 15 wt % of the DVB were prepared at 1/1 in St/St ratio. In comparison, highly crosslinked monodispersed and smooth-surfaced PS particles containing up to 70 wt % of the DVB were effectively prepared at 0/1. 5% weight loss of the PS particles determined by TGA occurred from

353.3 to 389.6°C and the degree of swellability in toluene increased from 113 to 101% as the DVB concentration increased from 10 to 70 wt %, implying increased thermal stability and solvent resistance due to the increase of the crosslink density. This study demonstrates that the seeded semicontinuous process, primarily with the starved condition at the second stage, is an efficient way to obtain highly crosslinked, monodispersed PS particles. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3092–3102, 2010

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

INTRODUCTION

There have been strong demands for highly crosslinked polymer particles^{1–9} with superior heat resistance, solvent resistance, and mechanical strength because of their extensive applications such as column packing materials,⁶ protein synthesis and biomedical applications,⁷ polymer-supported catalysis, spacer for display uses, conductive ball, etc. Therefore, the development of a novel technique for the preparation of monodispersed highly crosslinked polymer particles becomes an important research subject.

Dispersion polymerization^{10–15} is an important polymerization method to prepare monodispersed micron-sized polymer particles. However, when the crosslinking agent was used in the dispersion polymerization some problems^{5,13,14,16,17} have encountered, including loss of control of particle size, broadening of the size distribution, odd-shaped particles, and coagulation of the polymer particles in the reaction. Many articles^{13,14,16,17} report that dis-

persion polymerization failed when the crosslinking agents less than 0.5 wt % based on the monomer present. Recently, some studies^{5,16–24} on how to overcome flocculation and deformation in dispersion polymerization have been reported. Generally, the crosslinking agents interfere with the sensitive particle nucleation step causing flocculation and deformation. Winnik et al.²⁰ reported that uniform micron-sized crosslinked PS particles with 1 wt % of ethyleneglycoldimethacrylate (EGDMA) could be obtained by delayed addition of crosslinking agent after the end of the nucleation stage in the dispersion polymerization. Lee and Lee^{23,24} also reported that crosslinked monodisperse poly(methylmethacrylate) particles with 7–8 wt % of DVB were successfully made by seeded batch and semicontinuous dispersion polymerizations in which 5 μm poly(methylmethacrylate) seeds were used to avoid the sensitive nucleation stage in the presence of the crosslinking agent. In our previous study,²⁵ the preparation of crosslinked micron-sized polystyrene particles was intensely investigated by seeded batch and delayed addition by batch dispersion polymerization, uniform crosslinked PS particles with 7–20 wt % of DVB were successfully prepared. The semicontinuous process^{24,26} is of considerable technique in controlling the polymer compositions,

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TABLE I
Semicontinuous Process

Ingredients	Wt (%)	Amount (g)	
		Flask ^a	Feeder ^b
ST	12.58	–	15
EtOH	86.04	97.47	5.13
PVP K-30	1.25	1.5	–
AIBN	0.13	–	0.15
DVB	–	–	00.45
Total	100	98.97	(0–3 wt %) ^c 20.28

^a Polymerization condition: 70°C, 125 rpm for 24 h.

^b Feeding time: 6–12 h.

^c Based on St monomer.

polymerization rates, polymer morphology, etc. and in producing industrial synthetic copolymers. This study focuses on obtaining the highly crosslinked uniform PS particles using seeded semicontinuous dispersion polymerization by investigating the effect of the polymerization factors such as addition point and feeding time of the crosslinking agent, concentration of the crosslinker, polymerization temperature, and Styrene (in 2nd stage)/Styrene (in PS seed) ratio on the particle size and morphology. In addition, semicontinuous process and delayed addition process are also examined.

EXPERIMENTAL

Materials

Styrene (St, Junsei) was washed with 10 wt % aqueous NaOH solution to remove inhibitor. Divinylbenzene (DVB 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 pyrrolidone) (PVP K-30, Junsei) was used as a steric stabilizer.

Dispersion polymerization

Semicontinuous process

Table I shows the reaction condition for the dispersion polymerization of styrene by semicontinuous process. The mixture of EtOH (97.47 g) and PVP k-30 (1.5 g) were added to a 250 mL four-neck reaction flask equipped with a reflux condenser, thermocouple, nitrogen purging inlet, and anchor type stirrer, and the temperature was raised gradually to 70°C under a nitrogen atmosphere at 125 rpm. When the temperature reached 70°C, the mixture of St (15 g), DVB 0–0.45 g (0–3 wt %), EtOH (5.13 g), and AIBN

(0.15 g) were added continuously for 6–12 h to the reaction flask using a microfeeder and the reaction was allowed to proceed for 24 h.

Delayed addition by semicontinuous process

In this study, the delayed addition process in which the crosslinker added after the nucleation period was used. The mixture of EtOH (97.47 g) and PVP k-30 (1.5 g) was first added into a reaction flask and the temperature was raised gradually to 70°C under a nitrogen atmosphere at 125 rpm. When the temperature reached 70°C, the zero reaction time was defined with the addition of the mixture of St (15 g) and AIBN (0.15 g). The mixture of DVB (0.0525–0.15 g, 0.35–1 wt %) and EtOH (5.13 g) was then added continuously for 6–15 h using a microfeeder 3–360 min after the start of the polymerization. The polymerizations were carried out at 70°C with postreaction up to a total of 24 h.

Seeded semicontinuous process

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

Seeded semicontinuous process. Table III shows the standard for the preparation of crosslinked PS particles by the seeded semicontinuous dispersion polymerization. The PS seed latex (19.88 g) prepared as Table II was first charged to the reactor at 125 rpm and purged with nitrogen, and then the temperature was gradually raised. When the reactor temperature reached 70°C, the monomer mixture was added continuously for 3–15 h with postreaction at 70°C up to a total of 24 h. The St/St ratio indicates the ratio of the amount of styrene used in 2nd stage to 1st stage

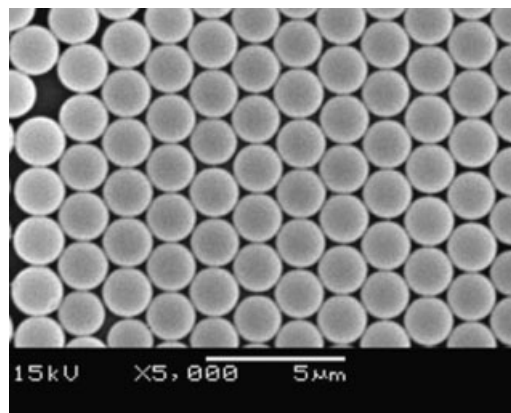


Figure 1 Scanning electron micrograph of PS seed particles.

TABLE II
Preparation of PS Seed^a

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

^a Polymerization condition: 70°C, 125 rpm for 24 h.

(PS seed preparation), which was divided into 1/1 and 0/1 in this study. The DVB concentration used in this experiment was in the range of 0–100 wt % based on the total amount of styrene used in 1st and 2nd stages.

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 overnight. Then sample was sputter-coated with gold and examined at 15 kV. The particle size of the latexes was measured with photographs and the particle size distribution (PSD) were also determined as the ratio of the number (\overline{D}_n) and weight (\overline{D}_w) average diameters as follows²⁷:

$$\overline{D}_n = \frac{\sum_{i=1}^N D_i}{N} \quad (1)$$

$$\overline{D}_w = \frac{\sum_{i=1}^N D_i^4}{\sum_{i=1}^N D_i^3} \quad (2)$$

Where, N is the total number of particles counted and D_i is the diameter of particle i .

$$\text{PSD} = \frac{\overline{D}_w}{\overline{D}_n} \quad (3)$$

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/m in the temperature range from 25 to 700°C. All measurements were made under an N₂ gas flow rate of 50 mL/m.

The swellability of the crosslinked PS microspheres was determined by observing the change in

the number-average diameter between the maximum swelling point (\overline{D}_1) observed after 48 h and the dried, original particle (\overline{D}_0). The \overline{D}_1 kept basically unchanged after 12 h. 0.5 g of crosslinked PS particles was put into 5 mL toluene at room temperature, and then observed the change in the size and shape using an optical microscopy (OM, Leica DMLM) with time. The swellability of the particle was calculated as follows²¹:

$$\text{Swellability}(\%) = \frac{\overline{D}_1}{\overline{D}_0} \times 100$$

RESULTS AND DISCUSSION

Semicontinuous process

Table IV and Figure 2 show the morphology of the PS particles prepared with five different DVB concentrations (0–3 wt %) according to the polymerization as shown in Table I.

Figure 1 shows the SEM micrograph of the mono-dispersed PS seed particles, prepared by the batch process as shown in Table II in which the stable particle growth taken place after the short nucleation. In comparison, secondary nucleation with broad size distribution was observed in the semicontinuous process due to the long nucleation time and continuous secondary nucleation [Fig. 2(A)].

The raisin-like particles [Fig. 2(B)] were prepared by the semicontinuous process with 6 h feeding at 0.35 wt % of the DVB concentration, whereas 1.5 μm uniform PS particles were formed with 9 h feeding [Fig. 2(C)]. The raisin-like particles were also observed with 9 h feeding at 0.5 [Fig. 2(D)], 1 wt % of the DVB and 12 h feeding at 1, 3 wt % [Fig. 2(E)]. The deformation and flocculation of particles were found at more than 3 wt % of the DVB.

It is also known that DVB is more reactive than styrene ($r_{St}/r_{m-DVB} = 0.6/0.88$, $r_{St}/r_{p-DVB} = 0.15/$

TABLE III
Standard Recipe for Seeded Semicontinuous Process (Amounts in grams)^a

Ingredients	1st Stage ^b PS seed	2nd Stage	
		1/1 ^c	0/1 ^c
St	2.5	2.5	0
EtOH	17.1	17.1	17.1
PVP K-30	0.25	–	–
AIBN	0.025	0.025	0.025
DVB	–	0–5 (0–100) ^d	0–2.5 (0–100) ^d

^a Polymerization condition: 70°C, 125 rpm for 24 h.

^b PS seed latex prepared in Table II.

^c St (in 2nd stage)/St (in PS seed) ratio.

^d wt % based on total amount of St monomer used in 1st and 2nd stages.

TABLE IV
Dispersion Polymerization by Semicontinuous Process^a

Sample	DVB concentration (wt %) ^b	Feeding time(h)	Particle morphology
A	0	6	Polydispersed and smooth-surfaced particles
B	0.35	6	Raisin-like particles
C	0.35	9	Monodispersed and smooth-surfaced particles
D	0.5, 1	9	Raisin-like particles
E	1, 3	12	and generation of secondary particles

^a Polymerization condition: 70°C, 125 rpm for 24 h.

^b Based on styrene monomer.

1.00) in copolymerization of St/DVB.^{19,20} Therefore, for the batch process DVB present at the initial stage of polymerization would react preferentially to make particle nuclei with crosslinked structure, resulting in polydispersed and raisin-like deformed particles.¹³ In comparison, the semicontinuous process in which the feeding time of crosslinker could be artificially controlled is more effective way to minimize the effect of the crosslinker compared to the batch process for smaller than 0.35 wt % of DVB. However, the semicontinuous process also has a limitation in preparation of the crosslinked monodis-

persed PS particles with more than 0.35 wt % of DVB. Accordingly, the delayed addition by semicontinuous process in which the addition point and feeding time of crosslinker are controllable was carried out.

Delayed addition by semicontinuous process

Effect of addition point and feeding time

Table V and Figure 3 represents the morphology of the PS particles prepared with different addition points and feeding times in the ranges of 0.35–3.0 wt % of DVB by the delayed addition process.

The raisin-like PS particles were observed for the polymerization in which 0.35 wt % of the DVB added 3 min (conversion: 8%) after the start of the reaction with 6 h feeding [Fig. 3(A)], which is the same shaped particles, prepared by the semicontinuous process as shown in Figure 2(B). 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%.¹⁵ However, the results obtained by the delayed addition do not follow the 15–16% as shown in Table V. When 0.35 wt % of the DVB was added between 15 and 180 min (conversion: 19–38%) after the start of the polymerization, polydispersed and smooth-surfaced particles were observed [Fig. 3(B)]. In comparison, monodispersed and smooth-surfaced PS particles could be prepared for

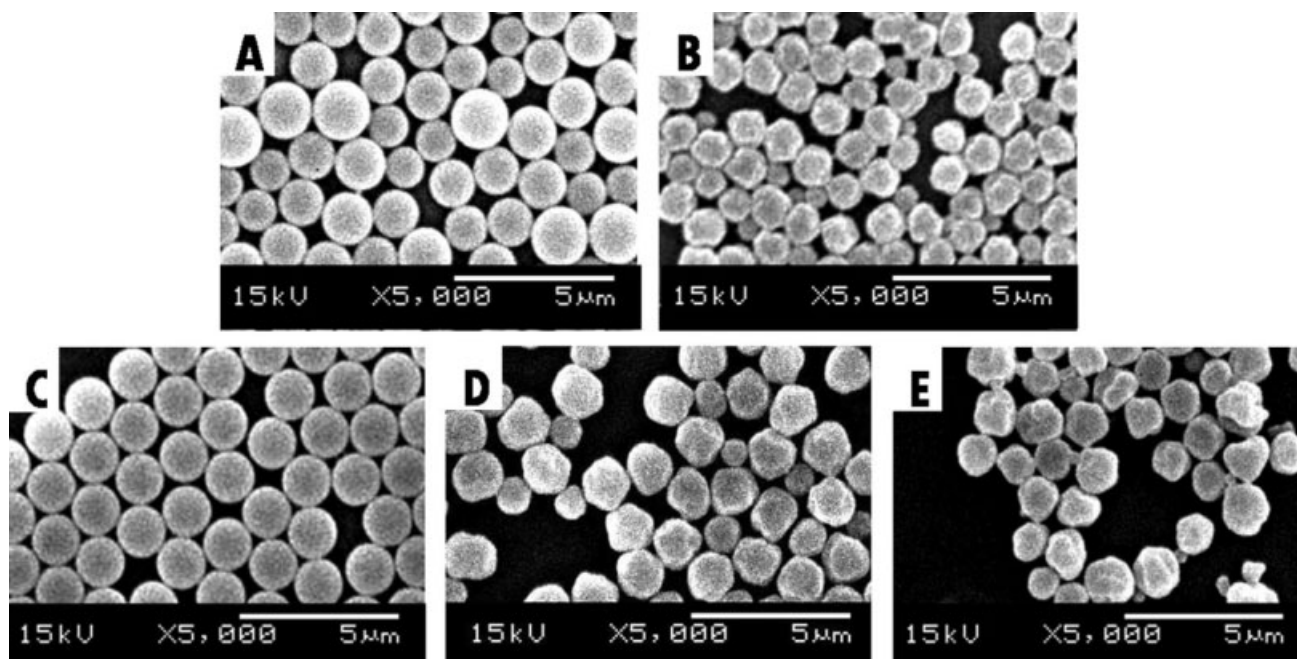


Figure 2 Scanning electron micrographs of PS particles prepared with different DVB concentrations by semicontinuous process [(A) 0 wt %, (B) 0.35 wt % for 6 h-feeding, (C) 0.35 wt % for 9 h-feeding, (D) 0.5 wt % for 9 h-feeding, (E) 1 wt % for 12 h-feeding].

TABLE V
Dispersion Polymerization by Delayed Addition Process^a

	DVB (wt %) ^b	Addition point (min) ^c	Feeding time (h)	\overline{D}_n (μm)	Conversion (%)	Particle morphology
A	0.35	3	6	–	8	Raisin-like particles
B	0.35	15–180	6	–	19–38	Polydispersed and smooth-surfaced particles
C	0.35	240	6	1.9	58	Monodispersed and smooth-surfaced particles
D	0.5	240	9	1.9	62	
E	1	240	9	–	–	Raisin-like particles
F	1	360	9	–	–	Polydispersed and smooth-surfaced particles
G	1	360	12	2.0	70	Monodispersed and smooth-surfaced particles
H	2	360	12	–	–	Raisin-like particles and generation of secondary particles
I	3	360	12	12	–	
J	3	360	15	–	85	Raisin-like particles

^a Polymerization condition: 70°C, 125 rpm for 24 h.

^b wt % of DVB based on St monomer.

^c The addition time of DVB after the beginning of the reaction.

240 m (conversion: 58%) after the start of the reaction [Fig. 3(C)].

1.9 μm monodispersed crosslinked PS particles were prepared by adding 0.5 wt % of the DVB with 9 h feeding at 240 m (conversion: 62%) after the start of the reaction [Fig. 3(D)]. 2.0 μm monodispersed and smooth-surfaced PS particles [Fig. 3(G)] were also obtained by adding 1 wt % of the DVB for 12 h feeding 360 m (conversion: 70%) after the start of the reaction, whereas polydispersed PS particles were

prepared with 9 h feeding. Particle deformation and secondary particles were observed for 3 wt % of the DVB with 15 h feeding 360 m after the beginning of the reaction [Fig. 3(J)].

Combining all the results, the delay addition method could not be identified the exact addition point of the DVB in this study. Even if the delayed addition process^{16,18–21} is more efficient way in artificially controlling the addition point of crosslinker than the semicontinuous process, the identification

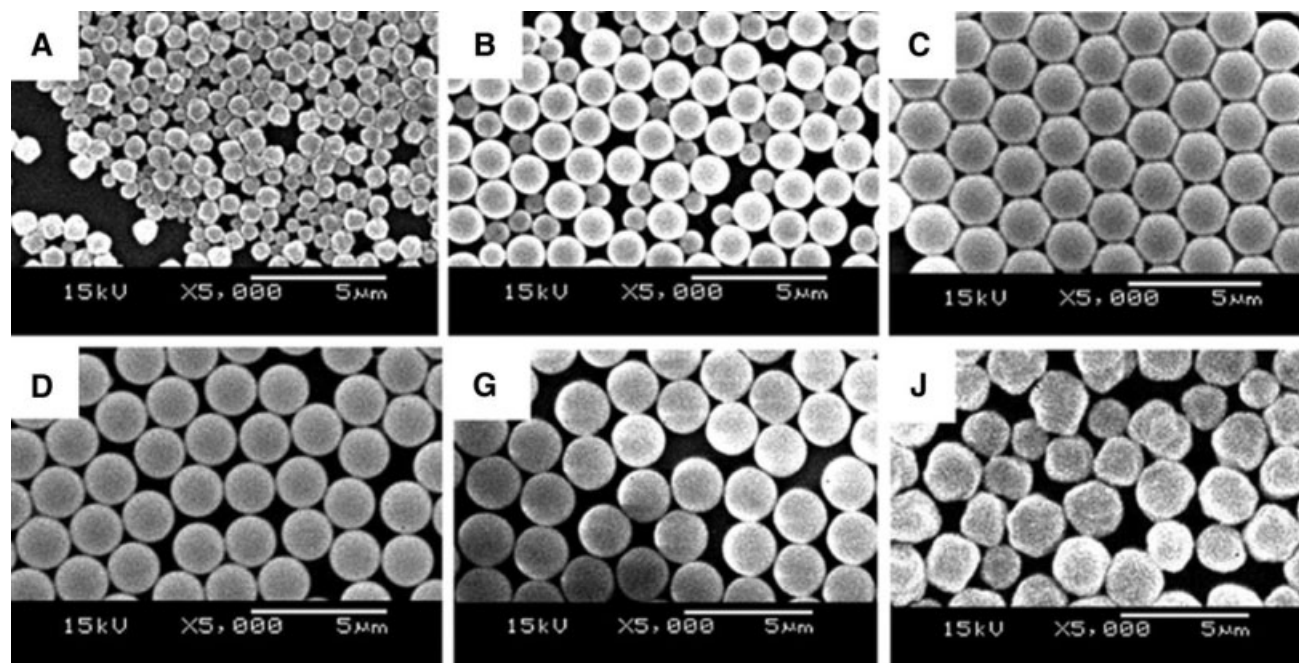


Figure 3 Scanning electron micrographs of PS particles prepared by delayed addition with semicontinuous process [(A) 3 m, (B) 15 m, (C) 240 m at 0.35 wt % DVB for 6 h-feeding, (D) 240 m at 0.5 wt % DVB for 9 h-feeding, (G) 360 m at 1 wt % DVB for 12 h-feeding, (J) 360 m at 3 wt % DVB for 15 h-feeding].

TABLE VI
Effect of Feeding Time^a

	St/St ratio ^b	DVB ^c (wt %)	Feeding time (h)	\bar{D}_n (μm)	PSD	Particle morphology
A	1/1	10	3	2.4	–	Heavily dented particles
B	1/1	10	6	2.3	1.001	Dimpled particles on the surface
C	1/1	10	9	2.3	1.002	Dimpled particles on the surface
D	1/1	10	12	2.3	1.002	Monodispersed and
E	1/1	10	15	2.3	1.002	smooth-surfaced particles

^a Polymerization condition: 70°C, 125 rpm for 24 h.

^b St (in 2nd stage)/St (in PS seed) ratio.

^c wt % of DVB based on total amount of st monomer used in 1st and 2nd stages.

of the exact addition point of the DVB for the preparation of the highly crosslinked monodispersed PS particles seems very difficult because of the complicated relationships with feeding time, concentration of crosslinker, reaction temperature, etc.

Seeded semicontinuous process

In the present work, preparation of highly crosslinked monodispersed PS particles by seeded semicontinuous process was carried out using the

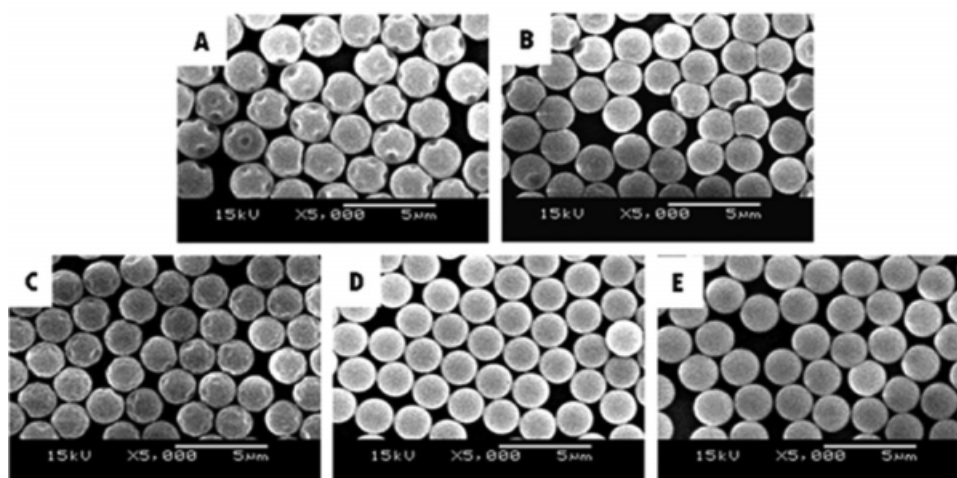
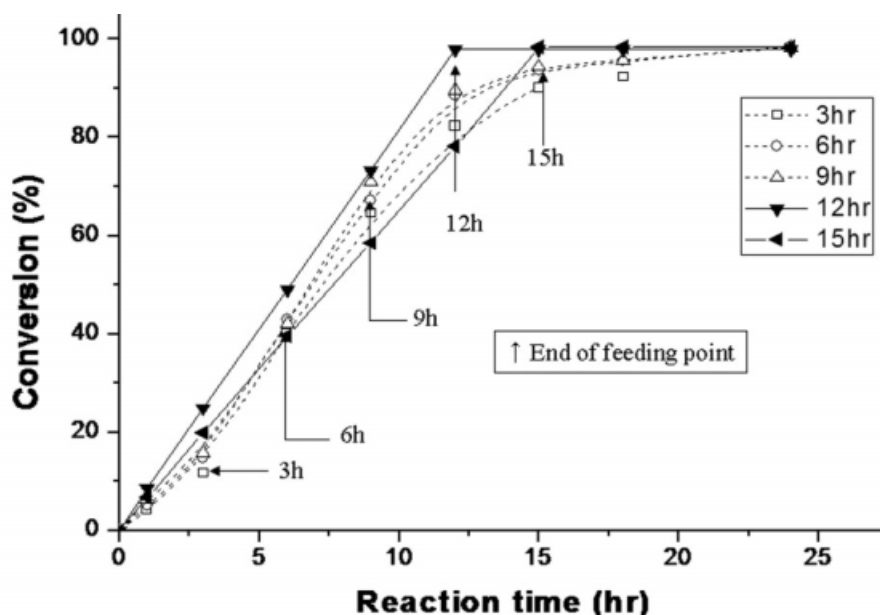


Figure 4 Scanning electron micrographs and the time-conversion curves of crosslinked PS particles prepared with five different feeding times for 10 wt % of the DVB by seeded semicontinuous processes [(A) 3, (B) 6, (C) 9, (D) 12, (E) 15 h].

TABLE VII
Effect of DVB Concentration^a

	St/St ratio ^b	DVB (wt %) ^c	\overline{D}_n (μm)	PSD	Particle morphology
A	1/1	10, 15	2.2	1.001	Monodispersed and smooth-surfaced particles
B	1/1	20	2.3	–	Dimpled particles on the surface and generation of secondary particles
C	1/1	25	–	–	Coagulation
D	0/1	50, 65	2.1–2.3	1.001	Monodispersed and smooth-surfaced particles
E	0/1	70	2.4	1.002	Monodispersed and dimpled particles on the surface
F	0/1	75	2.5	–	Dimpled particles on the surface and generation of secondary particles

^a Feeding time: 12 h, Polymerization condition: 70°C, 125 rpm for 24 h.

^b St (in 2nd stage)/St (in PS seed) ratio.

^c wt % of DVB based on total amount of st monomer used in 1st and 2nd stages.

ready-made 1.9 μm PS seed particles under the variation of St (in 2nd stage)/St (in PS seed) ratio, feeding time, concentration of DVB, and polymerization temperature. The polymerizations performed in the experiment were all over 95 wt % conversion.

Effect of feeding time

Table VI and Figure 4 show the particle size, size distribution, morphology, and the time-conversion curves of the PS particles prepared with five different feeding times for 10 wt % of the DVB in the St/St ratio of 1/1.

It was observed that for 10 wt % of the DVB concentration, monodispersed smooth-surfaced PS particles were prepared with longer than 12 h of feeding time [Fig. 4(D,E)], while dimpled particles were observed with 6–9 h feeding [Fig. 4(B,C)]. Heavily dented particles on the surface also appeared with less than 3 h of feeding time [Fig. 4(A)]. Generally, the deformation of the particles became severe with decreasing the feeding time in this system. In this study, the time-conversion curves for the monomer feeding times for more than 12 h were found to be linear, indicating that the reactions were allowed to proceed under the monomer-starved condition in

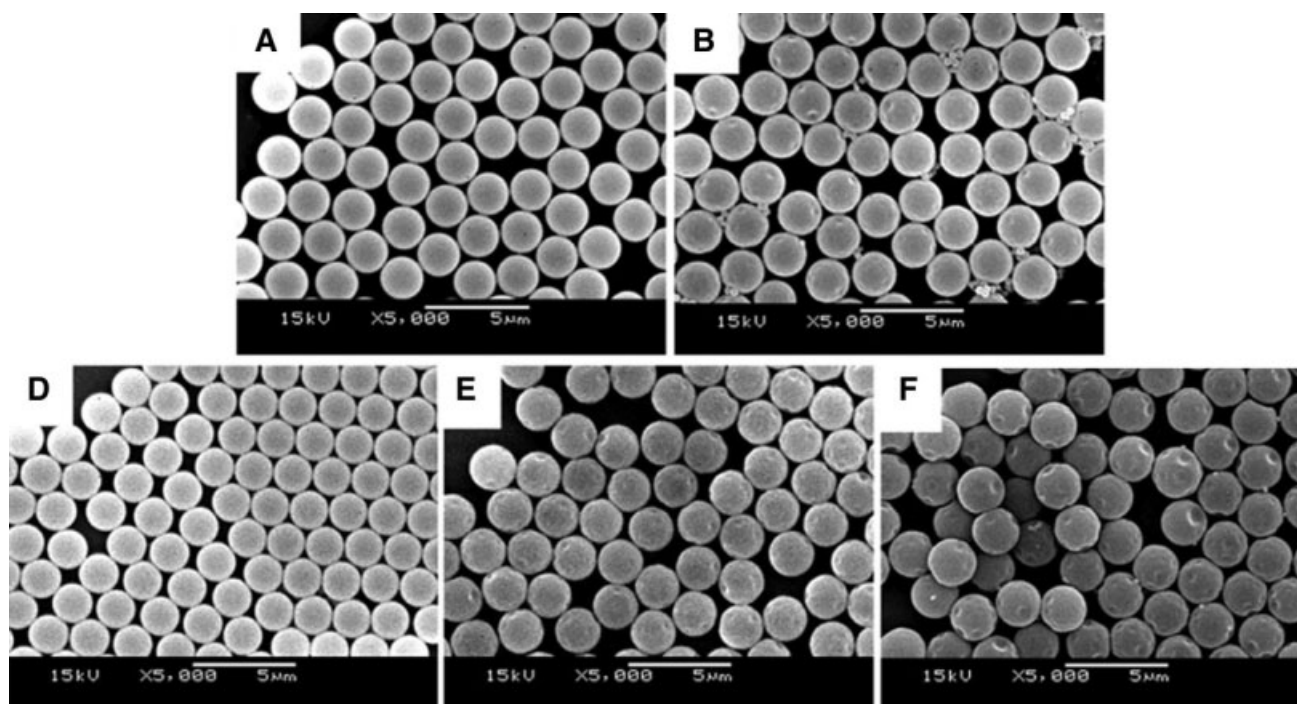


Figure 5 Scanning electron micrographs of crosslinked PS particles prepared with 12-h feeding at different DVB concentrations and St/St ratio [(A) 15 wt % (B) 20 wt % at 1/1, (D) 65 wt % (E) 70 wt % (F) 75 wt % at 0/1 in St/St ratio].

TABLE VIII
Effect of Polymerization Temperature^a

	St/St ratio ^b	DVB (wt %) ^c	Pol ⁿ temp (°C)	\bar{D}_n (μm)	PSD	Particle morphology
A	1/1	15	60, 70	2.3	1.002	Monodispersed and smooth-surfaced particles
B	1/1	15	75	2.3	1.001	Monodispersed and dimpled particles on the surface
C	1/1	20	60	2.4	1.002	Monodispersed and dimpled particles on the surface
D	0/1	60	70, 75	2.3	1.002	Monodispersed and smooth-surfaced particles
E	0/1	70	60	2.4	1.002	Monodispersed and dimpled particles on the surface
F	0/1	70	70	2.4	1.003	Monodispersed and dimpled particles on the surface
G	0/1	70	75	2.4	–	Dimpled particles on the surface and generation of secondary particles
H	0/1	75	60	2.5	–	Dimpled particles on the surface and generation of secondary particles

^a Feeding time: 12 h, Polymerization condition: 70°C, 125 rpm for 24 h.

^b St (in 2nd stage)/St (in PS seed) ratio.

^c wt % of DVB based on total amount of st monomer used in 1st and 2nd stages.

which the monomer consumes as fast as it enters the reactor without accumulation of monomer, resulting in monodispersed PS particles with more homogeneous crosslink structure.

In comparison, the time-conversion curves for less than 9 h showed nonlinearity, indicating that the reactions were in the monomer-flooded condition in which the residual monomer is accumulated throughout the reaction and at the final stage the composition drift occurred with conversion, resulting in odd-shaped deformed particles with secondary nucleation or coagulum as the case of the batch process.²⁵

Effect of DVB concentration

Table VII and Figure 5 show the particle size, size distribution, and particle morphology of the PS particles prepared with various DVB concentrations ranged from 10 to 75 wt % in 1/1 and 0/1 of St (in 2nd stage)/St (in PS seed) ratios.

2.2 μm monodispersed PS particles were prepared in the range of 10–15 wt % of the DVB at the St/St ratio of 1/1 [Fig. 5(A)], indicating the occurrence of facile polymerizations within the PS particles, while dimpled particles on the surface and secondary nucleated particles were observed with 20 wt % of the DVB Fig. 5(B)], indicating the occurrence of phase separation within the particles due to formation of a dense crosslinked network. Further increase of the DVB concentration to 25 wt % led to coagulation among the particles.

Monodispersed and smooth-surfaced PS particles were obtained in the range of 50–65 wt % of the DVB at the St/St ratio of 0/1 [Fig. 5(D)], whereas uniform particles with dimple were observed in the 70 wt % of the DVB [Fig. 5(E)]. Furthermore, the dented particles with secondary particles were generated at 75 wt % of the DVB [Fig. 5(F)]. In general, the crosslinked PS particles prepared at the St/St ratio of 0/1 contain much higher DVB concentration

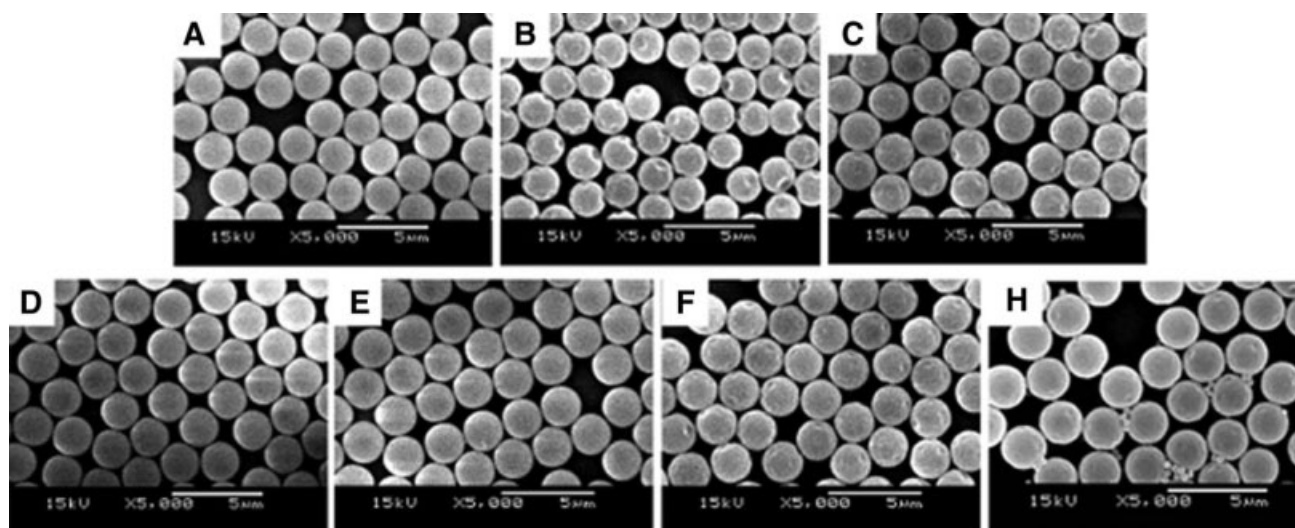


Figure 6 Scanning electron micrographs of crosslinked PS particles prepared with different polymerization temperatures [(A) 65°C (B) 75°C, 15 wt % DVB (C) 60°C, 20 wt % DVB at 1/1, (D) 70°C, 60 wt % DVB (E) 60°C (F) 70°C, 70 wt % DVB (H) 60°C, 75 wt % DVB at 0/1 in St/St ratio].

compared with those at the St/St ratio of 1/1 as shown in Table VII. The amount of monomer used in the second stage at the St/St ratio of 0/1 is very small (about 1/3.5 based on 65 wt % DVB) compared to that of 1/1 (St/St) ratio, which is only DVB itself. Therefore, the smaller amount of the DVB added at the St/St ratio of 0/1 makes infiltration of the DVB inside the PS seed particles more facile and the highly crosslinked PS particles are formed in the end with the occurrence of the stable crosslinking reaction inside the PS particles.

Effect of polymerization temperature

Table VIII and Figure 6 show the particle size, size distribution, and particle morphology of the PS particles prepared at four different polymerization temperatures (60–75 °C) under various DVB concentration in the St (in 2nd stage)/St (in PS seed) ratio of 1/1 and 0/1.

Monodispersed and smooth-surfaced PS particles containing 15 wt % DVB were prepared at the St/St ratio of 1/1, under polymerization temperature ranging from 60 to 70°C [Fig. 6(A)], whereas dimpled particles were generated at 75°C by phase separation due to the high reactivity of DVB [Fig. 6(B)]. Dimpled PS particles with narrow size distribution were effectively prepared at 20 wt % of the DVB concentration by reducing the polymerization temperature to 60°C [Fig. 6(C)].

Monodispersed and smooth-surfaced PS particles without generation of secondary particles containing up to 60 wt % DVB were prepared at the St/St ratio of 0/1, under polymerization temperature ranging from 70 to 75°C [Fig. 6(D)]. In comparison, monodispersed and smooth-surfaced PS particles were effectively prepared with 70 wt % of the DVB by reducing the reaction temperature at 60°C [Fig. 6(E)], whereas dimpled particles were obtained at 70°C [Fig. 6(F)]. In addition, dimpled particles and secondary particles were still present with 75 wt % of the DVB in spite of decreasing the reaction temperature to 60°C [Fig. 6(H)], and some coagulum along with many secondary particles was found with more than 80 wt % of the DVB.

The reactivity of DVB in the copolymerization of styrene with DVB in general increases with the polymerization temperature and vice versa. Therefore, the dispersion polymerizations performed at 75°C with more than 70 wt % of the DVB led to the formation of dense crosslinked structure of the PS particles which suppresses the swelling of the monomer mixture into the PS seed particles, resulting in the occurrence of the phase separation of the PS particles and a generation of small sized secondary particles after all. However, the crosslinking reaction becomes sluggish with decreasing the reaction tem-

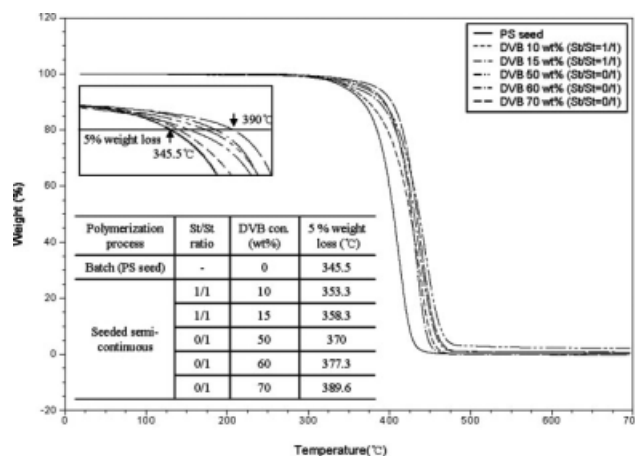


Figure 7 The thermogravimetry curves of crosslinked PS particles with different DVB concentrations from 0 to 70 wt %.

perature, the monomer added in the second stage is easily swollen into the PS seed particles and the subsequent stable crosslinking reaction inside the particles would lead to monodispersed PS particles. That is the reason why highly crosslinked monodispersed PS particles containing 70 wt % DVB were prepared in the reaction conditions at 60°C compared with that at 70°C in the St/St ratio of 0/1.

Characterization

Thermal stability

Figure 7 shows the TGA thermogram of crosslinked PS particles prepared with six different DVB concentrations ranging from 0 to 70 wt %. No obvious weight loss was observed in the temperature range between 50 and 300°C for all samples and 5% weight loss of PS seed particles occurred at 345.5°C. In comparison, 5% weight loss of crosslinked PS particles for the St/St ratio of 1/1 occurred from 353.3 to 358.3°C, with increasing concentration of DVB from 10 to 50 wt %. In addition, 5% weight loss for the St/St ratio of 0/1 occurred from 370 to 389.6°C, with increasing DVB concentration from 50 to 70 wt %. Generally, the thermal stability of crosslinked PS particles increased with increasing the DVB concentration. Especially, the crosslinked PS particles prepared with 70 wt % of the DVB at the St/St ratio of 0/1 provide the highest thermal stability as 389.6°C. This may be due to the formation of a dense crosslinked network structure²¹ within the particle, resulting from the addition of only DVB at the 2nd stage.

Swelling test

Table IX shows the swellability of the crosslinked PS particles prepared by various polymerization processes. PS seed particles were dissolved at once in

TABLE IX
Swellability of Crosslinked PS Particles

	Polymerization process	St/St ratio ^a	Feeding time (h)	DVB con. (wt %) ^b	Swellability ^c (%)
A	PS seed particles	–	–	0	Soluble
B	Semicontinuous process	–	9	0.35	Soluble
C	Delayed addition by semicontinuous process	–	12	1	Soluble
D	Seeded semicontinuous process	1/1	12	10	113.0
E	Seeded semicontinuous process	1/1	12	15	106.2
F	Seeded semicontinuous process	0/1	12	50	104.5
G	Seeded semicontinuous process	0/1	12	60	102.1
H	Seeded semicontinuous process	0/1	12	70	101.0

^a St (in 2nd stage)/St (in PS seed) ratio.

^b Based on total amount of St monomer used in 1st and 2nd stages.

^c Determined in toluene.

toluene [Table IX(A)]. PS particles prepared by the semicontinuous and the delayed addition processes were also easily dissolved [Table IX(B,C)]. The swellability of the particles prepared by the seeded semicontinuous process at the St/St ratio of 1/1, decreased from 113 to 106.2% with increasing the DVB concentration from 10 to 15 wt % [Table IX(D,E)]. In addition, the swellability of the particles at the St/St ratio of 0/1 decreased from 104.5 to 101% with increasing DVB concentration from 50 to 70 wt % [Table IX(F–H)]. The general trend is that the swellability of crosslinked PS particles improved with increasing the DVB concentration, as expected. PS particles with 70 wt % of the DVB in the St/St ratio of 0/1 show the lowest swellability as 101% due to the formation of a dense crosslinked network within the particles.

CONCLUSIONS

Various polymerization processes, such as semicontinuous, delayed addition, and seeded semicontinuous processes, were compared to prepare highly crosslinked monodispersed PS particles. Monodispersed and smooth-surfaced PS particles with 0.35 wt % of the DVB concentration were prepared at 70°C by the semicontinuous process with 9 h feeding. In comparison, monodispersed and smooth-surfaced PS particles with 1 wt % of the DVB were prepared by the delayed addition process in which the DVB was added slowly for 12 h feeding 360 m after the start of the reaction. However, 3 wt % of the DVB resulted in deformation and flocculation. In this study, to avoid the particle nucleation stage of the dispersion polymerization the seeded semicontinuous polymerizations using already-made 1.9 μm monodispersed PS seed were carried out under the various reaction conditions such as feeding time ranging from 3 to 15 h and concentration of the DVB

from 10 to 75 wt %, polymerization temperature from 60 to 75°C, and St (in 2nd stage)/St (in PS seed) ratio of 0/1 and 1/1. Monodispersed PS particles with 15 and 70 wt % of DVB could be successfully made at 60°C under the monomer starved condition with 12 h feeding in the St/St ratio of 1/1 and 0/1, respectively. This study also showed 5% weight loss of the crosslinked PS particles prepared by the seeded semicontinuous process increased from 353.3 to 389.6°C and the swellability decreased from 113 to 101% with increasing DVB concentration from 10 to 70 wt % and the PS particles prepared with 70 wt % of DVB in the St/St ratio of 0/1 provided the highest thermal stability and the lowest swellability. These results confirm that the seeded semicontinuous process with the starved condition is a more efficient way to obtain highly crosslinked, monodispersed PS particles than any other traditional processes.

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References

- Denizli, A.; Kesencib, K.; Aricac, Y. *React Funct Polym* 2000, 44, 235.
- Tuncel, A.; Tuncel, M.; Ergun, B.; Alagoz, C.; Bahar, T. *Colloid Surf A: Phys Eng Asp* 2002, 197, 79.
- Kawaguchi, S.; Winnik, M. A. *Macromolecules* 1995, 28, 1159.
- Sheu, H. R.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A: Polym Chem* 1990, 28, 629.
- Hattori, M.; Sudol, E. D.; El-Aasser, M. S. *J Appl Polym Sci* 1993, 50, 2027.
- Liang, Y. C.; Svec, F.; Frechet, J. M. J. *J Polym Sci Part A: Polym Chem* 1995, 33, 2639.
- Cui, Y. J.; Zhao, M.; Tang, X. Z.; Luo, Y. P. *Biomaterials* 2004, 25, 451.
- Li, W. H.; Stover, H. D. H. *J Polym Sci Part A: Polym Chem* 1999, 27, 2899.
- Bondar, Y. V.; Kim, H. J.; Lim, Y. J. *J Appl Polym Sci* 2007, 104, 3256.
- Almog, Y.; Reich, S.; Levy, M. *Br Polym J* 1982, 14, 131.

11. Lok, K. P.; Ober, C. K. *Can J Polym Sci Polym Chem* 1985, 63, 209.
12. Tuncel, A.; Kahraman, R.; Piskin, E. *J Appl Polym Sci* 1993, 50, 303.
13. Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A: Polym Chem* 1986, 24, 2995.
14. Shen, S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1994, 32, 1087.
15. Lee, K. C.; Wi, H. A. *J Polym Sci Part A: Polym Chem* 2008, 46, 6612.
16. Tomson, B.; Rudin, A.; Lajoie, G. *J Polym Sci Part A: Polym Chem* 1995, 33, 345.
17. Yang, W. L.; Yang, D.; Hu, J. H.; Wang, C. C.; Fu, S. K. *J Polym Sci Part A: Polym Chem* 2001, 39, 555.
18. Zhang, H. T.; Huang, J. X.; Jiang, B. B. *J Appl Polym Sci* 2002, 85, 2230.
19. Cui, H.; Chen, H.; Qu, R.; Wang, C.; Ji, C.; Sun, C.; Zhou, W.; Yu, M. *J Appl Polym Sci* 2007, 107, 3909.
20. Song, J. S.; Winnik, M. A. *Macromolecules* 2005, 38, 8300.
21. Cao, M.; Tong, B.; She, J.; Dong, Y.; Zhi, J. *J Appl Polym Sci* 2008, 109, 1189.
22. Gong, T.; Wang, C. C. *J Mater Sci* 2008, 43, 1926.
23. Lee, K. C.; Lee, S. Y. *Macromol Res* 2007, 15, 244.
24. Lee, K. C.; Lee, S. Y. *Macromol Res* 2008, 16, 293.
25. Lee, K. C.; Wi, H. A. *J Appl Polym Sci*, to appear.
26. Lee, K. C.; El-Aasser, M. S.; Vanderhoff, J. W. *J Appl Polym Sci* 1991, 42, 3133.
27. Kiakamjornwong, S.; Kongsupapsiri, C. *Polym Int* 2000, 49, 1395.