

Synthesis of crosslinked polystyrene particles by seeded batch polymerization with monomer absorption

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Abstract: A highly crosslinked, monodispersed polystyrene(PS) particle was prepared by a seeded batch dispersion polymerization with a monomer absorption method. Prior to polymerization, 1.9 μm monodispersed PS seed particles were treated under an optimum condition of monomer absorption. The effects of divinylbenzene(DVB) concentration and polymerization temperature were examined for styrene(in PS seed)/styrene(in the second stage) mass ratio of 1:1 in the medium range of EtOH/water mass ratio of 100/0–80/20 and 2.3 μm uniform crosslinked PS particles containing 15%–20% (mass fraction) DVB were prepared at 60–70 °C. The results show that monomer absorption before the second stage of polymerization is more effective to prepare highly crosslinked monodispersed PS particles.

Key words: crosslinked polystyrene particle; seeded batch dispersion polymerization; monomer absorption; divinylbenzene (DVB)

1 Introduction

Micron-sized monodispersed polymer particles are used in a wide variety of scientific and technological applications with high-value-added materials, such as ion-exchangers, medical and chemical application as absorbents and polymer-supported catalyst[1–3]. Especially, there are strong demands for highly crosslinked polymer beads with superior heat resistance, solvent resistance, mechanical strength to serve as a spacer for display panel, slip property improves for plastic film and conductive ball[4–5]. The recent typical technique, which was used in the preparation of monodispersed beads with micrometer diameter, is a dispersion polymerization, which was extensively studied[6–10]. This process is very attractive for large-scale preparation of such particles. Recently, the dispersion polymerization was studied to overcome the problem of flocculation and deformation from the influence of crosslinker[9–16]. However, there are no reports on the seeded dispersion process through the monomer absorption procedure prior to polymerization in the presence of crosslinker.

In this work, the preparation of highly crosslinked, monodispersed polystyrene (PS) particles was carried out

under the variation of divinylbenzene (DVB) concentration, polymerization temperature and styrene (in PS seed)/styrene(in the second stage) ratio through the monomer absorption procedure using the 1.9 μm PS seed particles before the seeded dispersion polymerization.

2 Experimental

2.1 Materials

Styrene (Junsei) was washed with 10% (mass fraction) 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 prior to use. 2,2'-Azobis (isobutyronitrile) (AIBN, Junsei) was recrystallized from methanol. All other materials were used without further purification. As a polymerization medium, ethanol (EtOH, Daejung chemical) and distilled deionized-water were used. Poly (vinyl pyrrolidone) (PVP K-30, Junsei) was used as a steric stabilizer.

2.2 Seeded batch polymerization

2.2.1 Preparation of polystyrene(PS) seed

Fig.1 shows the SEM micrograph for the PS seed particles prepared by the recipe as listed in Table 1.

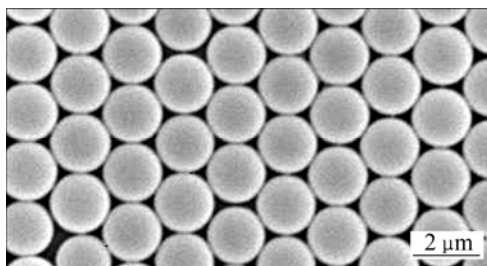


Fig.1 SEM micrograph of PS seed particles

Table 1 Preparation condition of PS seed

Ingredient	w/%	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 cycle/min for 24 h

The PS seed latex particles are all uniform in 1.9 μm-diameter and the polymerization shows higher than 96% (mass fraction) conversion with a negligible coagulum.

2.2.2 Seeded batch polymerization with monomer absorption

Table 2 lists the standard recipe for the second stage polymerization after the monomer absorption procedure. Before the polymerization, as the monomer absorption process, 10 mL bottle (2.2 cm×5.1 cm) as a reactor was placed in a shaker operating at 100 cycle/min in a constant temperature water bath at 25 °C for 1 h. The DVB concentration used in this experiment was 0–100% (mass fraction) based on the total amount of styrene used in the first and second stages as listed in Table 2.

Table 2 Standard recipe for seeded batch polymerization with monomer absorption

Ingredient	Seeded batch polymerization with monomer absorption/g	
	1st (PS seed latex)	2nd(seeded batch pol ¹⁾)
ST	0.46	0.46 ¹⁾
EtOH	3.1	3.1 ³⁾
Water	0–0.775 ²⁾	0–0.775 ³⁾
PVP K–30	0.046	–
AIBN	0.004 6	0.004 6
DVB	–	0–0.92 ⁴⁾

1) Styrene(in PS seed)/styrene(in 2nd stage) mass ratio of 1/1; 2) 0–0.775 g water was post-added to the PS seed mixture; 3) EtOH/water mass ratio of 100/0–80/20; 4) mass fraction of DVB (1–100) based on total amount of styrene(in PS seed)/styrene(in 2nd stage) monomer.

2.2.3 Characterization

The particle size, size distribution and morphology of the resulting dispersion were analyzed using scanning electron microscope (SEM, Jeol Jsm 6400) and an optical microscope (OM, Leica LMDM). The dispersion was coated with the aluminum stud and dried at room temperature overnight. Then the sample was sputter-coated with gold and examined at 15 kV. The particle size distribution (PSD) was determined as the ratio of the number ($\overline{D_n}$) and mass ($\overline{D_m}$) average diameters as follows:

$$\overline{D_n} = \sum_{i=0}^N D_i / N \quad (1)$$

$$\overline{D_m} = \sum_{i=0}^N D_i^4 / \sum_{i=0}^N D_i^3 \quad (2)$$

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

$$\text{PSD} = \overline{D_m} / \overline{D_n} \quad (3)$$

3 Results and discussion

3.1 Optimum condition for monomer absorption

3.1.1 Effect of ethanol(EtOH)/water ratio

Fig.2 shows the SEM micrographs of PS particles prepared at five different EtOH/water mass ratios (100/0–80/20, mass fraction) through the monomer absorption procedure according to the recipe as listed in Table 2. For the seeded polymerizations without monomer absorption procedure, 2.3 μm-sized uniform PS particles (Fig.2(a)) were prepared at mass ratio of EtOH to water of 100/0, while small sized secondary particles were prepared at EtOH/water mass ratio of 95/5–80/20 (Figs.2(b), (c)). On the other hand, in the monomer absorption process carried out at 25 °C for 1 h, the monodispersed crosslinked PS particles were made in all EtOH/water mass ratio ranging in 100/0–80/20 (Figs.2(d)–(f)).

It is in general expected that the diffusion rate of non-polar monomers like styrene or divinylbenzene (DVB) into PS seed particles increases with increasing polarity in the medium. Without monomer absorption, therefore, the monomer mixtures were diffused easily into the PS seed particles with increasing amount of water in the medium. It is also known that the DVB is more reactive than the styrene in the copolymerization of the St/DVB ($r_{St}/r_{m-DVB} = 0.6/0.88$, $r_{St}/r_{p-DVB} = 0.15/1.00$)¹³. Therefore, the DVB located near the surface of the PS seed particles would react preferentially to make a dense

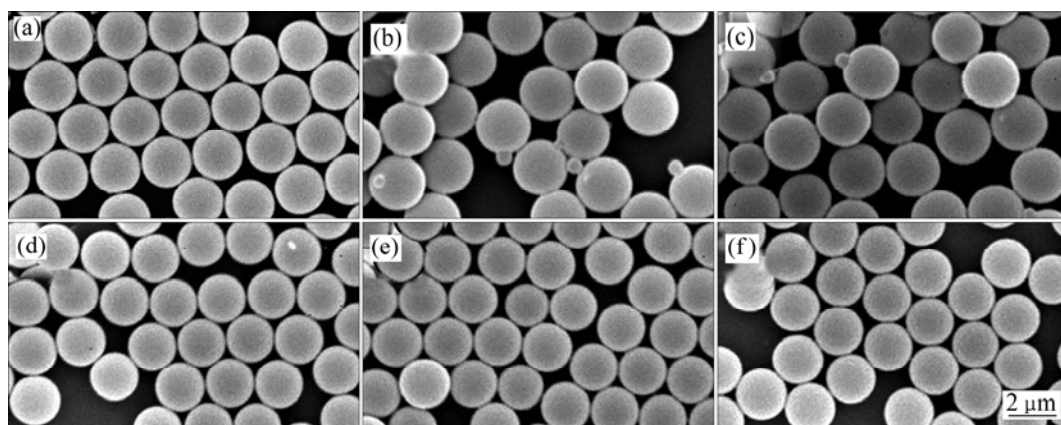


Fig.2 SEM images of PS particles prepared with different EtOH/water mass ratios: (a), (d) 100/0; (b), (e) 95/5; (c), (f) 80/20; (a), (b), (c) By non-absorption; (d), (e), (f) By monomer absorption at 25 °C, 100 cycle/min for 1 h

crosslinked structure. However, the crosslinking on the surface of the PS particles could suppress the swellability of the monomer mixture into the PS seed particles, which resulted in a generation of secondary particles due to the dispersion polymerization of the monomer present in the medium with increasing polarity of the medium. On the other hand, in the case of the monomer absorption, the polymerization started after the sufficient diffusion of monomer mixture into the PS seed, resulted in monodispersed crosslinked PS particles throughout the medium range of EtOH/water mass ratio of 100/0–80/20.

3.1.2 Effects of absorption time

Table 3 and Fig.3 show the particle size, particle morphology and SEM micrographs of the PS particles prepared at EtOH/water mass ratio of 95/5 with the absorption time ranging from 0 to 24 h.

Table 3 Effect of monomer absorption time

EtOH/water mass ratio	Absorption time/h	$\overline{D_n} / \mu\text{m}$	PSD	Particle morphology
95/5	0	2.2	–	Generation of secondary particles
95/5	1	2.3	1.004	Monodispersed & Smooth surface particles
	3	2.3	1.004	
95/5	6	–	–	Deformed particles (twin and triplet shape)
	12	–	–	
	24	–	–	
	24	–	–	

Without monomer absorption procedure(0 h), small sized secondary particles were observed (Fig.3(a)). On the other hand, in the case of the monomer absorption for 1–3 h, 2.3 μm monodispersed PS particles were

produced (Figs.3(b), (c)). However, small amount of twin or triplet shaped particles were observed in the monomer absorption longer than 6 h (Figs.3(d)–(f)). This is because the stabilization ability of the steric stabilizer is weak due to the long swelling time. In the present study, monomer absorption for 1–3 h was found to be the optimum condition in which monodispersed crosslinked PS particles were made without formation of any secondary particles.

3.1.3 Effects of styrene(in PS seed)/styrene(in the second stage) mass ratio

Table 4 and Fig.4 show the particle size, particle morphology and SEM micrographs of the PS particles prepared in the range of styrene(in PS seed)/styrene(in the second stage) mass ratio of 1/1–1/3 with monomer absorption at 25 °C for 1 h.

Table 4 Effect of styrene(in PS seed)/styrene(in 2nd stage) mass ratio

EtOH/water mass ratio	St/St ratio ¹⁾	$\overline{D_n} / \mu\text{m}$	PSD	Particle morphology
100/0	1/1	2.3	1.003	Monodispersed and smooth surface particles
	1/1.5	2.6	–	
100/0	1/2	2.9	–	Generation of secondary particles
	1/3	3.4	–	

1) Styrene(in PS seed)/styrene(in 2nd stage) mass ratio.

In the case of styrene/styrene mass ratio of 1:1 with monomer absorption, 2.3 μm monodispersed crosslinked PS particles (Fig.4(a)) were prepared in the medium of EtOH/water mass ratio of 100/0. However, in the case of

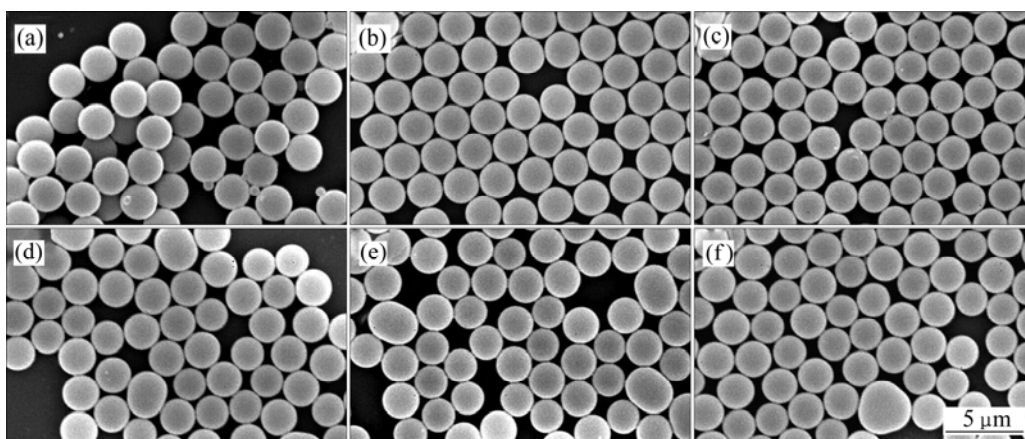


Fig.3 SEM photographs of PS particles prepared at different absorption times and 25 °C, 100 cycle/min in EtOH/water mass ratio of 95/5: (a) 0; (b) 1 h; (c) 3 h; (d) 6 h; (e) 12 h; (f) 24 h

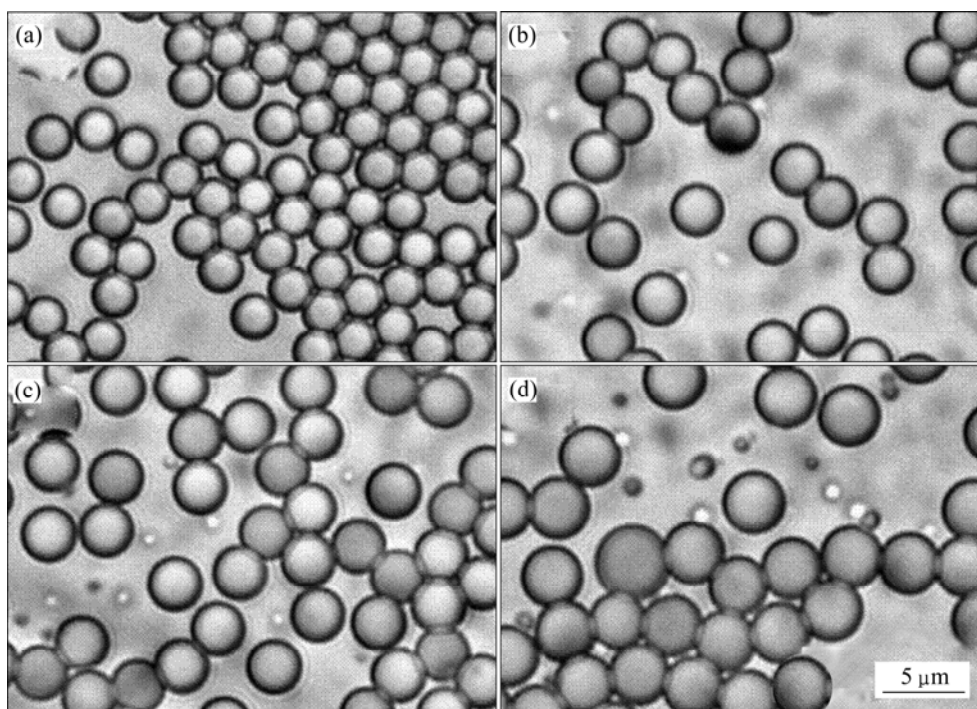


Fig.4 Optical micrographs of PS particles prepared at four different styrene(in PS seed)/styrene(in the second stage) mass ratios with monomer absorptions in different EtOH/water mass ratio of 1/1(a), 1/1.5(b), 1/2(c), 1/3(d)

1/1.5–1/2, large numbers of small sized secondary particles (Figs.4(b), (c)) were formed due to the excess styrene monomer present in the medium. Furthermore, in the case of 1/3, some coagulum along with many secondary particles was found (Fig.4(d)). The similar results to that in the case of EtOH/water mass ratio of 100/0 were also observed in EtOH/water mass ratio of 95/5–80/20.

3.2 Seeded batch polymerization with monomer absorption

3.2.1 Effects of DVB concentration

Table 5 and Fig.5 show the particle size, particle

morphology and SEM micrographs of the PS particles prepared in the DVB concentration of 10%–25% (mass fraction) with monomer absorption at 25 °C for 1 h.

For 10% (mass fraction) of the DVB, 2.3 μm monodispersed crosslinked PS particles (Fig.5(a)) were made through the entire medium range of EtOH/water mass ratio of 100/0–80/20. In the case of 15% and 20% (mass fraction) of the DVB, uniform particles were found in the range of EtOH/water mass ratio of 100/0–95/5 (Fig.5(b)) and 100/0 (Fig.5(c)), respectively. However, in EtOH/water mass ratio of 90/10 secondary nucleated small particles were generated in the range of 15%–20% (mass fraction) of the DVB (Fig.5(d), (e)).

Some coagulum with many secondary particles were also found in 25% (mass fraction) of the DVB (Fig.5(f)).

3.2.2 Effects of polymerization temperature

Table 6 and Fig.6 show the particle size, particle morphology and SEM micrographs of the PS particles prepared in the DVB concentration of 15%–20% at two different polymerization temperatures (60 and 70 °C) with monomer absorption at 25 °C for 1 h.

For the polymerization temperature at 60 °C, 2.3 μm smooth surfaced uniform PS particles with 15%

DVB were made in the entire range of EtOH/water mass ratio of 100/0–80/20 (Fig.6(a)). Monodispersed PS particles with 20% DVB were also observed in the medium range of EtOH/water mass ratio of 100/0–90/10 (Fig.6(c)). On the other hand, in the case of at 70 °C, uniform PS particles with 15% DVB were made in the range of EtOH/water mass ratio of 100/0–95/5 (Fig.6(b)). However, for 20% DVB monodispersed PS particles were made only in the medium of EtOH/water mass ratio of 100/0 (Fig. 6(d)).

Table 5 Effect of DVB concentration

w(DVB)/% ¹⁾	EtOH/water mass ratio	$\overline{D_n}$ /μm	PSD	Particle morphology
10	100–80/20	2.3	1.002	Monodispersed and smooth surface particles
15	100/0–95/5	2.4	1.003	
20	100/0	2.5	1.003	
15	90/10–80/20	–	–	Generation of secondary particles
20	95/5–80/20		–	
25	100/0–80/20	–	Generation of secondary particles and coagulation	

1) Mass fraction of DVB based on total amount of styrene(in PS seed)/styrene(in 2nd stage) monomer.

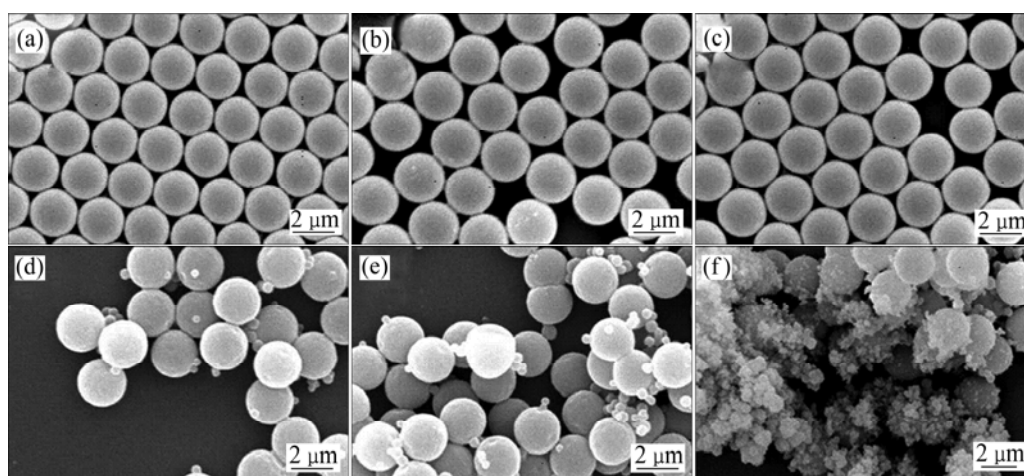


Fig.5 SEM photographs of crosslinked PS particles prepared at different DVB concentrations by seeded batch polymerization with monomer absorption: (a) 10% DVB; (b) 15% DVB; (c) 20% DVB; (a), (b), (c) At EtOH/water mass ratio of 100/0; (d) 15% DVB; (e) 20% DVB; (f) 25% DVB; (d), (e), (f) At EtOH/water mass ratio of 90/10

Table 6 Effect of polymerization temperature

w(DVB)/% ¹⁾	EtOH/water mass ratio	Pol ⁿ temp/°C	$\overline{D}_n / \mu\text{m}$	PSD	Particle morphology
15	100/0–80/20	60	2.4	1.003	Monodispersed and smooth surface particles
15	100/0–95/5	70	2.4	1.004	
20	100/0–90/10	60	2.5	1.004	
20	100/0	70	2.5	1.005	

1) Mass fraction of DVB based on total amount of styrene(in PS seed)/styrene(in 2nd stage) monomer.

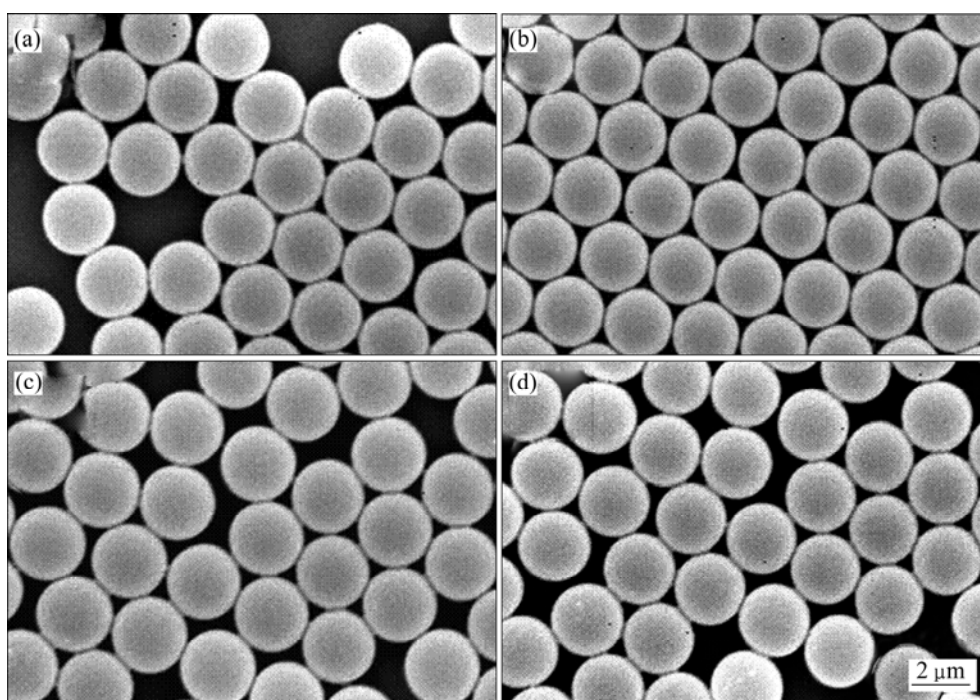


Fig.6 SEM photographs of crosslinked PS particles prepared at two different polymerization temperatures by seeded batch polymerization with monomer absorption: (a) 60 °C, (b) 70 °C at 15% (mass fraction) DVB (EtOH/water mass ratio of 100/0); (c) 60 °C, (d) 70 °C at 20% (mass fraction) DVB (EtOH/water mass ratio of 90/10)

4 Conclusions

1) The highly crosslinked, mono- dispersed PS particles were made by seeded batch dispersion polymerization after the monomer absorption procedure. It was found that the monomer absorption for 1–3 h at 25 °C and 100 cycle/min for styrene(in PS seed)/styrene (in the second stage) mass ratio of 1/1 were the optimum conditions in which monodispersed smooth surfaced crosslinked PS particles were made.

2) At 70 °C, the polymerization temperature under the monomer absorption, 2.3 μm uniform crosslinked PS particles with 15% and 20% (mass fraction) DVB were prepared in the medium of EtOH/water mass ratio of 100/0–90/10 and 100/0, respectively. On the other hand, at 60 °C monodispersed PS particles at the same concentration were made in the medium range of EtOH/water mass ratio of 100/0–80/20 and 100/0–90/10, respectively.

3) Monomer absorption before the seeded polymerization is more effective and versatile to prepare highly crosslinked monodisperse PS particles.

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