

# Preparation of Highly Crosslinked Monodisperse Poly(styrene-*co*-divinylbenzene) Microspheres by Two-Stage Dispersion Polymerization

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**ABSTRACT:** Monodisperse poly(styrene-*co*-divinylbenzene) microspheres crosslinked with different concentrations of divinylbenzene were synthesized by two-stage dispersion polymerization in ethanol dispersion medium with poly(*N*-vinyl pyrrolidone) as a stabilizer and 2,2'-azobisisobutyronitrile as a radical initiator. The microsphere size, size distribution, surface morphology, and structure were characterized by a particle analyzer, a scanning microscope and IR spectroscopy. The effect of the adding time, the adding rate, and the concentration of crosslinker on the size, size distribution, and shape of the resulting particles

were also investigated. Highly crosslinked monodisperse microspheres with diameters from 2 to 4  $\mu\text{m}$  were obtained. The SEM characterization showed that the resulting microspheres had spherical shapes with smooth surfaces. The obtained microspheres have good resistance to solvent whether at ambient or heating temperatures and are thermally stable. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1189–1196, 2008

**Key words:** microspheres; micron-sized; crosslinking; dispersion polymerization; postaddition

## INTRODUCTION

There has been considerable interest for the past 2 decades in the preparation of polymer particles, mainly due to their wide variety of applications such as in standard calibration, biomedical examinations, chromatographic fillers, spacers, ink additives, and catalytic substrates.<sup>1–5</sup> Suspension polymerization is suitable for polymer particles with a size range from 20  $\mu\text{m}$  to 2 mm. The size of the polymer particles prepared by emulsion polymerization is usually between 50 and 300 nm, and the polymer has colloidal stability because of ionic or nonionic surfactants. Particles ranging from 1 to 10  $\mu\text{m}$  with a narrow size distribution were prepared, either by Vanderhoff's successive seeding method<sup>6,7</sup> or by Ugelstad's two-stage swelling method.<sup>8,9</sup> However, both approaches are rather complicated and time-consuming. Dispersion polymerization as a new approach to the preparation of micron-size particles was discovered in 1970s.<sup>10</sup> Dispersion polymerization process is simple, just in a single batch and the obtained microspheres are monodisperse under favorable circumstances. Now varieties of micro-

spheres with different functional groups have been prepared in different media by dispersion polymerization.<sup>11–16</sup>

For some special applications such as column packing materials for chromatography, spacers for liquid crystal displays, and so on, highly crosslinked monodisperse microspheres having enough strength and solvent-resisting are desirable. Stover and coworkers<sup>17,18</sup> used precipitation polymerization to obtain micron-size highly crosslinked microspheres with different fraction of monomer with divinylbenzene. Huang and coworkers<sup>19,20</sup> used distillation-precipitation polymerization to prepare monodisperse poly(divinylbenzene) microspheres. There are also much research about the preparation of crosslinked microspheres, but the crosslinker concentration were less than 5 wt % relative to the monomer by dispersion polymerization.<sup>21–24</sup> When crosslinker concentration continued to be increased, odd-shaped particles were obtained with a broad size distribution and flocculation or coagulation of the dispersion was resulted.<sup>25,26</sup>

The present work is aimed at reporting on the preparation of highly crosslinked micron-size polystyrene microspheres with monodisperse size distribution by two-stage dispersion polymerization. The effect of the adding time, the adding rate and the concentration of crosslinker on the size, size distribution, and shape of the resulting particles are also investigated.

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**TABLE I**  
Standard Recipe for the One-Stage Dispersion Copolymerization

Materials		Weight (g)	Part (wt %)
Monomer	Styrene	10.0	10 <sup>a</sup>
Crosslinker	DVB	0.1	1 <sup>b</sup>
Medium	Ethanol	88.6	88.6 <sup>a</sup>
Stabilizer	PVP	1.0	10 <sup>b</sup>
Initiator	AIBN	0.3	3 <sup>b</sup>

<sup>a</sup> Based on total media weight.

<sup>b</sup> Based on monomer weight.

## EXPERIMENTAL

### Materials

Styrene was supplied as analytical grade by Beijing Chemical Reagents, Beijing, China. Divinylbenzene (DVB, 80% mixture of meta and para isomers) was available from Fluka Chemical. Both styrene and DVB was washed with 5% aqueous sodium hydroxide and distilled water and then dried over anhydrous magnesium sulfate prior to use, while the styrene was purified further by vacuum distillation before polymerization. 2,2-Azobis(2-methylpropionitrile) isobutyronitrile (AIBN, analytical grade, available from Beijing Chemical Reagents) was recrystallized from anhydrous ethanol. Poly(*N*-vinylpyrrolidone) (PVP, molecular weight: 40,000 g mol<sup>-1</sup>) and other reagents were also analytical grade and used as received without further purification.

### One-stage dispersion polymerization

The standard recipe for the one-stage dispersion copolymerization of styrene with DVB in anhydrous ethanol was listed in Table I. A typical procedure: PVP, AIBN, DVB, and styrene were dissolved in anhydrous ethanol in a three-neck 250-mL round-bottom flask equipped with a condenser and a gas inlet. The mixture was stirred at 120 rpm under N<sub>2</sub>. Then the flask was placed in 70°C water bath. The reaction was kept for 12 h with continuous stirring and nitrogen purge. After the polymerization, the mixture was poured into anhydrous ethanol (200 mL). The particles were separated by centrifugation and washed with ethanol and distilled water three times separately. The obtained particles were dried under vacuum at ambient temperature.

### Two-stage dispersion polymerization

The standard recipe for the two-stage dispersion copolymerization of styrene with DVB in anhydrous ethanol was listed in Table II. A typical procedure: PVP, AIBN, and styrene were dissolved in anhydrous ethanol about 75% of the total amount in a

three-neck 250-mL round bottom flask equipped with a condenser and a gas inlet. The mixture was stirred at 120 rpm under N<sub>2</sub>. Then the flask was placed in 70°C water bath. At the fourth hour after the beginning of the reaction, DVB in the remaining 25% anhydrous ethanol was dropped slowly to the reaction mixture (at 0.13 mL/min). The total reaction time was 12 h. The latter procedures were same as the treatment of the products obtained from the one-stage polymerization.

### Characterization techniques

The morphology of produced particles was observed using a scanning electron microscope (JSM-35c). The particle size and size distribution were defined by a particle size analyzer (CILAS 1064). Some of the SEM size data reflect the averages of about 100 particles each, which are calculated by the following formula:

$$D_n = \sum_{i=1}^k n_i D_i / n_i$$

$$D_w = \sum_{i=1}^k n_i D_i^4 / n_i D_i^3$$

$$PDI = D_w / D_n$$

where  $D_n$  is the number-average diameter,  $D_w$  is the weight-average diameter,  $N$  is the total number of the measured particles, and  $D_i$  is the particle diameters of the determined microspheres. PDI is the polydispersity index.

FTIR spectra was measured using a FTIR spectrophotometer (IR Prestige-21, Shimadzu). The thermogravimetric analyses of the particles were performed on Netzsch TG 209 thermogravimetric analyzer, at a heating rate of 10°C/min in nitrogen atmosphere.

Conversions were determined with a gravimetric method. The vials containing all the ingredients (10 mL) were extracted from the thermostated water bath with the time-intervals. Promptly, after adding a drop of 1% hydroquinone solution, the vials were

**TABLE II**  
Standard Recipe for the Two-Stage Dispersion Copolymerization

Materials		Weight (g)	
		First stage	Second stage
Monomer	Styrene	10	0
Crosslinker	DVB	0	4
Medium	Ethanol	63	22
Stabilizer	PVP	1.0	0
Initiator	AIBN	0.5	0

**TABLE III**  
The Experiment Remarks for the One-Stage Dispersion Polymerization with Different Concentrations of DVB and PVP

Sample	PVP (wt %) <sup>a</sup>	DVB (wt %) <sup>a</sup>	Remark
x-1	10	0.5	Monodisperse
x-2	10	0.6	Most of particles no longer spherical
x-3	10	1.0	Flocculate lightly
x-4	10	2.0	Coagulum after 1 h
x-5	10	5.0	Coagulum after 0.5 h
x-6	10	10.0	Coagulum immediately
y-1	20	0.5	Monodisperse
y-2	20	0.6	Some particles no longer spherical
y-3	20	1.0	Flocculate after 1 h
y-4	20	2.0	Coagulum after 1.5 h
y-5	20	5.0	Coagulum after about 45 min
y-6	20	10.0	Coagulum after 5 min

<sup>a</sup> Based on monomer styrene weight.

quenched in ice water. Each sample was then dried under a vacuum at ambient temperature, until the weight change was less than 0.001 g. The conversion was calculated as follows<sup>26</sup>:

$$C_n = \frac{M_2 - M_1 \times (w_2 + w_3)}{M_1 \times w_1}$$

where,  $C_n$  is the calculated fractional conversion,  $M_1$  is the weight of the sample before drying,  $M_2$  is the weight of the sample after drying,  $w_1$  is the wt % of the monomers (Styrene and DVB),  $w_2$  is the wt % of the stabilizer, and  $w_3$  is the wt % of the initiator.

## RESULTS AND DISCUSSION

### One-stage dispersion polymerization

We carried out the one-stage dispersion copolymerization of styrene in the presence of four concentrations of DVB (0.5, 0.6, 1, and 1.5 wt % of DVB based on styrene). For the reactions in the presence of 0.5 and 0.6 wt % DVB, the reaction mixtures became cloudy and "milky" in less than 10 min. With a higher DVB content (1.5 wt %), flocculation occurred after only 5 min, and the amount of aggregates increased with the increasing of polymerization time. With 0.5 wt % DVB, the PS particles were monodisperse, and with 0.6 wt % DVB, the particles were no longer spherical. With 1.0 wt % DVB, the particles have irregular shapes. These results are similar to those reported by Tseng et al.<sup>3</sup>

PVP as steric stabilizer could prevent coalescence. The concentration of PVP was increased from 10 to 20 wt %, the crosslinked microspheres with higher than 10 wt % crosslinker based on styrene could not be obtained. Dispersion polymerization started in

the homogeneous phase, solvent could dissolve the monomers but precipitate the forming oligomers and polymers. The forming oligomers at the beginning of polymerization aggregated to form colloidal-stable particles. Such particles grew by capturing oligomers and monomers ultimately to form microspheres. So the solubility of solvent for the forming oligomers and polymers could influence the size of microsphere and the stability of dispersion polymerization. It could be adjusted by the polarity of solvent. We added different ratio of water into ethanol to change the polarity of medium, but we also could not get the expected microspheres. Those experiment remarks were listed in Tables III and IV.

From above experimental results, it can be seen that the concentration of crosslinker is the key factor to get a stable system for the dispersion polymerization to produce monodisperse microspheres with smooth surface. With the increasing of DVB concentration, more and more oligomers and monomers were captured by DVB during the nucleation stage that lead the initiated core could not be got, the system was coagulated quickly and the reaction could not be going on.

### Two-stage dispersion polymerization

Effect of adding DVB at different time

To avoid the influence of DVB on the nucleation stage, we delayed the addition of DVB at the time of 1, 3, 4, and 5 h after the reaction had begun. The average particle sizes, size distributions, and conversions obtained at the different time of adding DVB were listed in Table V. Figure 1 was the SEM images of DVB-crosslinked PS microspheres at different adding time. When adding DVB at 1 h after the reaction had begun, the particles were coagulum soon. Adding DVB at 3 h after the reaction had begun, doublet and triplet shaped particles were obtained. Adding DVB at the fourth hour, the obtained particles were spherical with a smooth surface and narrow size distribution [Fig. 1(a)]. But when adding at 5 h or more, polydisperse particles were obtained and the secondary initiated nucleation particles were observed [Fig. 1(b)]. It could be seen that adding DVB at 4 h after

**TABLE IV**  
The Experiment Remarks for the One-Stage Dispersion Polymerization with Different Polarity of the Solvent

Sample	CH <sub>3</sub> CH <sub>2</sub> OH:		Remarks
	H <sub>2</sub> O (v/v)		
w-1	95	: 5	Flocculate lightly after about 105 min
w-2	90	: 10	Flocculate after 120 min
w-3	80	: 20	Flocculate after about 85 min
w-4	70	: 30	Flocculate after 55 min
w-5	60	: 40	Flocculate after about 30 min

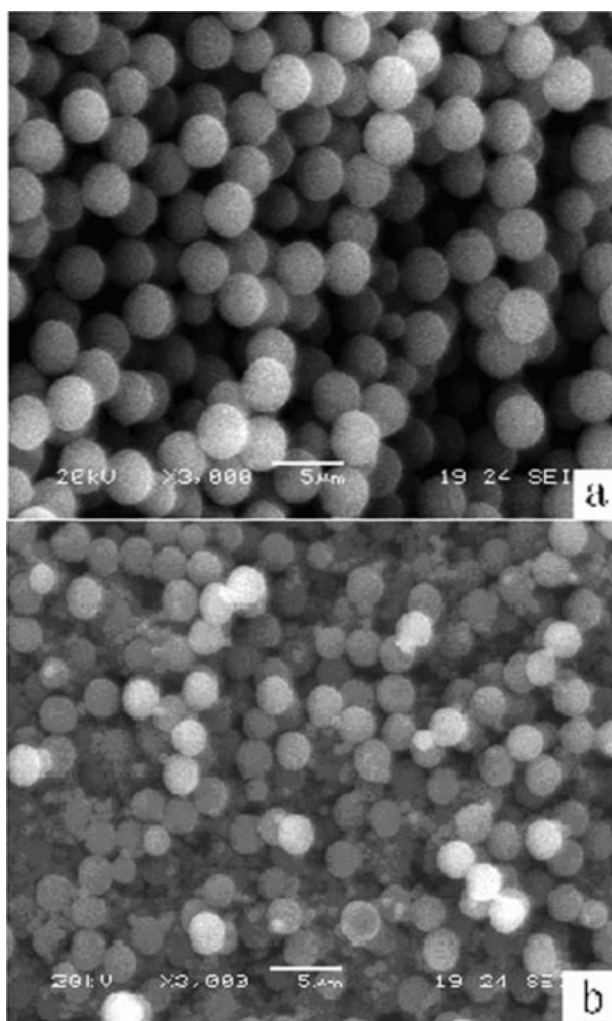
**TABLE V**  
The Effect of Adding Time of DVB on the Crosslinked Polystyrene Microspheres<sup>a</sup>

Time (h)	Particle size (μm)		PDI ( $D_w/D_n$ )	Conversion (wt %)
	$D_n$	$D_w$		
1	—	—	—	—
3	2.47	2.51	1.016	87.1
4	2.73	2.74	1.004	89.3
5	2.15	2.18	1.017	85.7

<sup>a</sup> The concentration of DVB based on styrene weight was 40 wt %, the adding rate of DVB was 0.13 mL/min.

the reaction begun is a proper time for this dispersion polymerization system to get highly crosslinked microspheres. It also can be induced that the core-shell microspheres were obtained.

On the basis of the latter conversion-time curve (Fig. 4), the concentration of monomer styrene at the different time of adding DVB could be calculated. At



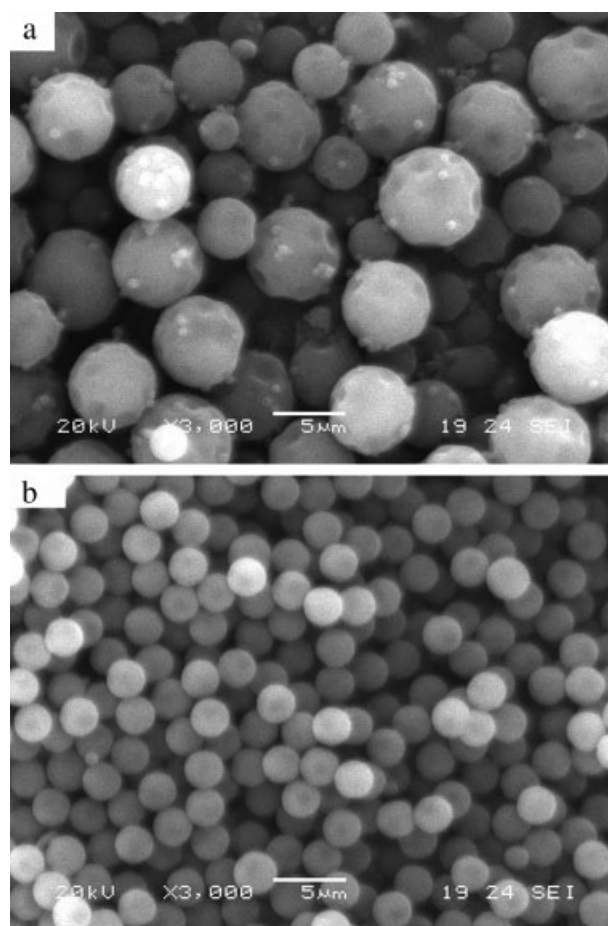
**Figure 1** SEM micrographs of DVB-crosslinked PS microspheres at different adding time. (a) 4 h and (b) 5 h.

**TABLE VI**  
The Effect of Adding Rate of DVB on the Crosslinked Polystyrene Microspheres<sup>a</sup>

Run	Rate (mL/min)	$D_n$ (μm)	$D_w$ (μm)	PDI
1	1	3.59	3.78	1.053
2	0.5	3.86	3.97	1.028
3	0.3	4.56	4.63	1.015
4	0.25	3.57	3.61	1.011
5	0.15	3.42	3.45	1.009
6	0.13	2.76	2.78	1.007

<sup>a</sup> The concentration of DVB based on styrene weight was 40 wt %, the adding time of DVB was at the fourth hour after the beginning of reaction.

the first hour, the concentration of monomer styrene was 9.31 wt %, and the system was in the nucleation stage, so with the adding of DVB, coagulum occurred. At the fifth hour, the concentration of monomer styrene was decreased to 4.27 wt %, the adding DVB could not capture more styrene, so DVB was initiated to form nucleation particles. It could be induced that the concentration of monomer styrene is also an important factor related to whether highly crosslinked core-shell microspheres could be prepared or not.



**Figure 2** SEM photographs of microspheres at different adding rate: (a) 0.5 mL/min; (b) 0.13 mL/min

### Effect of the addition Rate

In two-stage dispersion polymerization, when all the DVB were added in a lump at 4 h after the reaction had begun, the particle would soon coagulum and the polymerization could not continue, so we added DVB at different rate. The results of different addition rate of DVB were listed in Table VI. If the addition rate was more than 0.3 mL/min, the shapes of the particles are no longer spherical and have irregular shapes [Fig. 2(a)] The reason is that when the DVB was added quickly, more monomers and oligomers are connected by DVB for a certain time, and the captured amounts by the different areas of the formed particles were different, so the irregular crosslinked density were formed on the different areas of the particles. At the same time, polydisperse particles were obtained and some coagulum is yielded. It is due to the secondary nucleation and the agglomeration of particles in the part area in the medium.

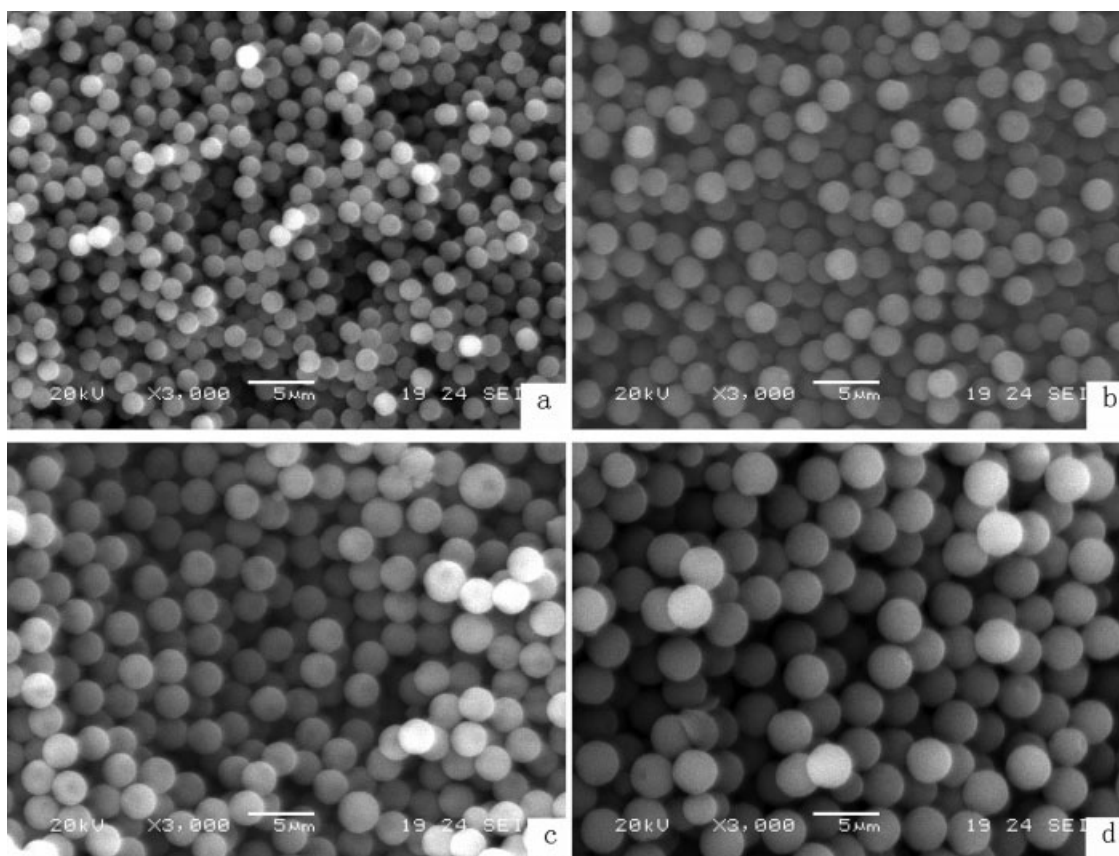
When the rate is slow enough at 0.15–0.13 mL/min, monodisperse particles were obtained and the particle prepared in Run 6 (Table VI) is more smooth and spherical [Fig. 2(b)]. Therefore, the slower the addition rate, the more stable the polymerization

and the better the monodispersity of the particles. When the adding rate of DVB is lower than 0.3 mL/min, the  $D_n$  of crosslinked polystyrene microspheres decreased with the decreasing of the adding rate. That is to say that the density of poly (DVB-styrene) shell increased with the decreasing of the adding rate of DVB.

From above experimental results, we can see that during the decreasing of adding rate of DVB from 1 mL/min to 0.13 mL/min, the obtained microspheres occurred the changes from odd-shape microspheres to monodisperse microspheres with smooth surface. Therefore the adding rate of DVB is very important factor related to whether crosslinked monodisperse microspheres could be obtained or not.

### Effect of DVB concentration

Crosslinked polystyrene particles were prepared with varying the concentrations of DVB from 10 to 40 wt % in ethanol solution at 70°C for 12 h. The SEM photographs of the particles with different concentrations of DVB from 10 to 40 wt % based on monomer weight were shown in Figure 3. The results were listed in Table VII. As the DVB concen-



**Figure 3** SEM photographs of crosslinked polystyrene microspheres with different concentrations of DVB: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, and (d) 40 wt % (based on monomer weight).

**TABLE VII**  
The Effect of DVB Concentration on the Crosslinked Polystyrene Microspheres<sup>a</sup>

[DVB] <sup>b</sup> (wt %)	Particle size ( $\mu\text{m}$ )		PDI ( $D_w/D_n$ )	Fractional conversion (wt %)	Temp. of 5% weight loss ( $^{\circ}\text{C}$ )
	$D_n$	$D_w$			
10	1.75	1.76	1.005	83.2	344
20	2.47	2.49	1.008	85.7	347
30	3.23	3.25	1.006	88.5	366
40	3.64	3.68	1.011	91.9	368

<sup>a</sup> The adding time of DVB was at the fourth hour after the beginning of reaction, the adding rate of DVB was 0.15 mL/min.

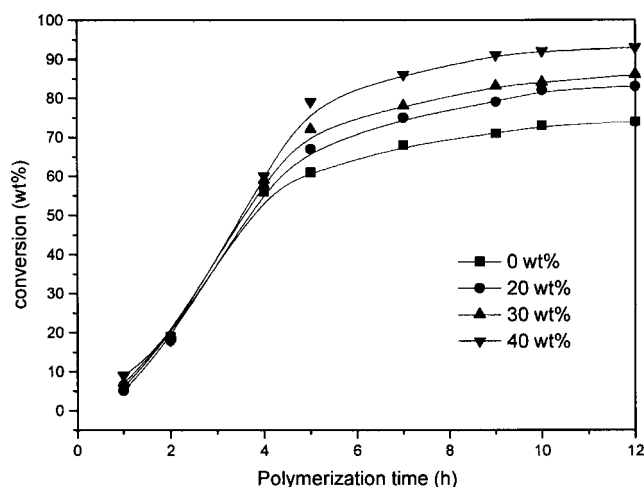
<sup>b</sup> The concentration of DVB based on styrene weight.

trations were increased from 10 to 40 wt % (relative to styrene monomer), the particle diameters were increased from 1.75 to 3.64  $\mu\text{m}$ . All of the afforded polymeric particles had narrow dispersion size with a polydispersity index at around 1.005–1.011.

On the basis of two-stage polymerization, we got core-shell polymer microspheres. The forming cores before adding DVB at the fourth hour were obtained under the same reaction condition, so their size and composition were same. With the adding of DVB the diameter of microsphere was increased. The higher DVB concentration, the bigger the highly crosslinked microspheres size.

#### Conversion

The conversion-polymerization time curves with changing crosslinker DVB concentration are shown in Figure 4. When the DVB content increases, the polymerization rate and the final monomer conversion increase. The conversion of the microspheres increased from 83.2 to 91.9%. DVB has a higher reactivity than styrene. It helps to decrease the activation

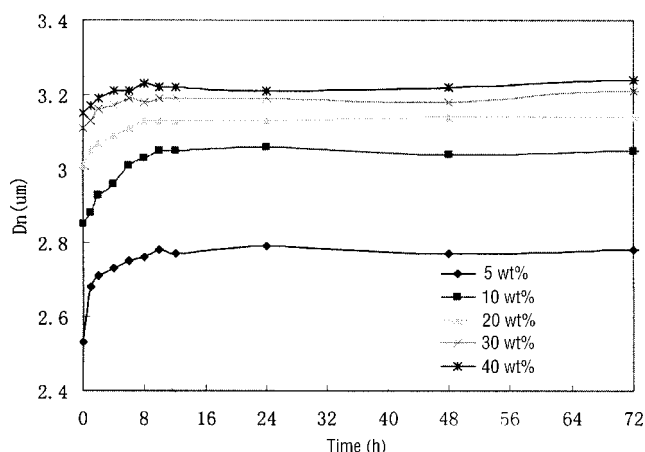


**Figure 4** The conversion-time curves of dispersion copolymerization under different DVB concentrations based on monomer weight from 0 to 40 wt %.

energy of polymerization and to increase the reaction rate. As the polymerization proceeds, the polymerization rate slows down. In the last stage, the number of nuclei does not rise any more, and the amount of monomers and crosslinking agent decreases. At the same time, the crosslinking density of the particles becomes higher.

#### Swelling ability and resistance to solvent

To investigate the property of the crosslinked microspheres in solvent, the swelling ability was measured. The synthesized microspheres were dipped in toluene at ambient temperature, and took out at different time and then observed the change in the size and shape. The results were showed in Figure 5. It can be observed that  $D_n$  of different DVB concentrations microspheres increases slowly with the increasing of dipping time, and after 10 h, the  $D_n$  keeps basically unchanged. As the content of DVB increased, the swelling speed is decayed. The swelling capacity ( $D/D_0$ ) after 16 h decreased from 1.10 to 1.02 with the increase of DVB concentrations from 5 to 40 wt % based on styrene. The shapes of microspheres are



**Figure 5** The effect of the swelling time in toluene on the diameters of microspheres with different DVB concentrations based on monomer weight from 5 to 40 wt %.

**TABLE VIII**  
The Weight Losing Ratio of the Obtained Microspheres with Different DVB Concentrations Based on Styrene

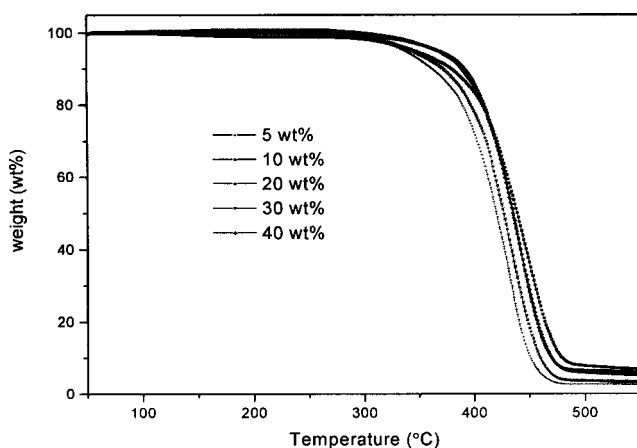
Sample	X10	X20	X30	X40
DVB (wt %)	10	20	30	40
WLR (wt %)	6.2	4.5	3.9	2.4

not changed. It is easily to understand that with the increasing of DVB concentrations the crosslink degree of the shell of microspheres increased, that could hinder the particle expansion. These results suggest that during the dispersion polymerization, the highly crosslinked polymer particles were hard to be swollen by the DVB and styrene. These findings combined with the observation of particle growth, imply that the particle growth mechanism is by the precipitation of polymer onto the nucleated particles.

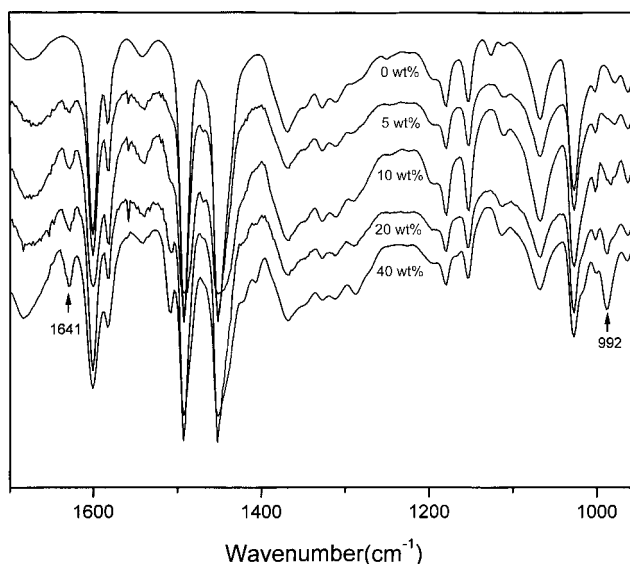
The resistance to solvent of resulting particles was also characterized with the weight losing ratio (WLR) of microspheres after being refluxed in 80 mL acetone for 12 h, the WLR results of different DVB concentrations microspheres are listed in Table VIII. The WLR decreases with the increase of DVB concentrations. When the concentration of DVB is 40 wt %, the WLR is 2.4 wt %. These results indicate that the synthesized microspheres have produced crosslinked networks around the surface of polystyrene core and they could effectively resistant to solvent.

#### Thermal stability

The thermal stability of microspheres with different DVB concentrations was measured by TGA. The thermogram was showed in Figure 6. No obvious weight loss was observed between 50 and 300°C for all samples. The temperatures of 5% weight loss of



**Figure 6** The thermogravimetry curves of crosslinked polystyrene samples with different DVB concentrations based on monomer weight from 5 to 40 wt %.



**Figure 7** The infrared spectra of crosslinked polystyrene samples with different DVB concentrations based on monomer weight from 0 to 40 wt %.

polystyrene microspheres with different DVB concentrations (listed in Table VII) increased from 344 to 368°C with the increase of DVB concentrations. It can be seen thermal stability increased obviously with the increasing of DVB concentrations.

#### IR analysis

The infrared spectra of the microspheres with different DVB concentrations by adding DVB at the fourth hour after the beginning of polymerization were shown in Figure 7. The absorption peaks appeared at about 1641  $\text{cm}^{-1}$  attributed to stretching vibration of ethenyl double bonds were found in the cross-linked polystyrene microspheres, but it was not found in the polystyrene microspheres without DVB. The absorption peak of the obtained microspheres at about 992  $\text{cm}^{-1}$  attributed to stretching vibration of 1-alkenes turned to weak with the decreasing of the DVB concentration from 40 to 5 wt %, and was disappeared when no DVB was added. That indicated that the double bonds of divinylbenzene were not all involved in the polymerization. There are also some double bonds of divinylbenzene existing in polymer microspheres.

#### CONCLUSIONS

Highly crosslinked monodisperse microspheres with 40 wt % DVB based on monomer could be obtained by two-stage dispersion polymerization. The SEM characterization showed that the resulting microspheres had spherical shapes and smooth surfaces. The narrow or mono-disperse polymer microspheres

were prepared by varying the adding time and the adding rate of DVB. When the adding rate of DVB is lower than 0.3 mL/min, the  $D_n$  of crosslinked polystyrene microspheres decreased with the decreasing of the adding rate. The resulting microspheres have good resistance to solvent whether at ambient or heating temperatures and are thermally stable.

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