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RESEARCH ARTICLE

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Mono-dispersed cross-linked polystyrene micro-spheres prepared by seed swelling polymerization method

Abstract A two-step swelling procedure was adopted to synthesize mono-dispersed and highly cross-linked poly (St-divinylbenzene) particles with PSt micro-spheres (1.80 μm in diameter). The PSt micro-spheres were prepared by a dispersion polymerization method and used as seeds. The effects of monomer concentration, ratio of ethanol to water, swelling reagents, crosslinking reagents, swelling temperature and agitation speed on particle size were investigated in detail. The morphologies and size distributions of these micro-spheres were examined by SEM and particle size analysis (PSA). The T_g of the micro-spheres was measured by DSC. The results indicate that the particles (6.20 μm in diameter) exhibit excellent mono dispersed property and high crosslinking degree when the concentration of the swelling reagent was 25%, the concentration of the cross-linking reagents was 23%, the swelling temperature was 30°C and the stirring speed was 150 r/min.

Keywords dispersion polymerization, seed swelling polymerization, mono-dispersed crosslinking polystyrene micro-spheres

In recent years, researches on micro-spheres have come into prominence for their wide applications in biomaterials, drugs and high-performance liquid chromatography (HPLC) fields. It is worth noting that high crosslinking, mono-dispersion and relatively large size of micro-spheres are especially important in their applications [1–4]. The preparation of excellent mono-dispersed micro-spheres with large diameters employ multiple steps and hard conditions [5]. Although mono-dispersed large size micro-spheres of up to 10 μm in diameter can be synthesized by dispersion polymerization in organic media, mono-dispersed micro-spheres with high crosslinking degree can not be produced due to gelatin formation [6,7]. The seed swelling polymerization technique is an effective method to prepare mono-dispersed micro-spheres with large diameters developed in recent years. The traditional seed swelling polymerization method consists of several steps. Acetone, which is introduced in the swelling process, influences the mono-dispersed property severely [8,9]. Report on the preparation of excellent mono-dispersed micro-spheres with large diameters has been scarce. In this study, large poly (St-divinylbenzene) particles with narrow size distribution and 23% crosslinking were prepared by a modified two-step seed swelling polymerization method in which the acetone was avoided. The quality of the mono-dispersed micro-spheres was improved while the process is kept relatively simple

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1 Experiments

1.1 Reagent and experiment

St and divinylbenzene (DVB) (55% divinyl monomer) were extracted with 10% aqueous sodium hydroxide and water, dried over anhydrous magnesium sulfate, distilled under vacuum and then kept in the refrigerator before use. Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were used after recrystallization. All other reagents were used as received.

The morphology of the micro-spheres was examined by use of a scanning electron microscope (JSM-6460LV). The diameter(d), standard deviation(δ) and distribution index was calculated by Eq. (1):

$$d=\sum_{i=1}^{n} d_i/n,\quad \delta=\left[\sum_{i=1}^{n}(d_i-d)^2\Big/(n-1)\right]^{1/2},\quad \varepsilon=\delta/d \quad (1)$$

where the d_i represents the single micro-sphere diameter and n represents the sample capacity ($n=20$).

The glass transition temperature was determined by DSC at a heating rate of 5°C/min under nitrogen. The particle size analysis was performed on a particle size analysis instrument (SA-CP3).

1.2 The preparation of PSt micro-spheres

A mixture of 1.362 g polyvinylpyrrolidone (PVP), 90 mL ethanol and 10 mL deionized water was placed in a 250 mL three-necked round bottom flask. 13.620 g St admixed with 0.136 g AIBN were added into the flask under nitrogen. The polymerization was carried out at 70°C for 10 h. The resulting product was treated with a typical centrifugal purification method and washed three times with ethanol. The purified seed was dried under vacuum for further use.

1.3 The preparation of high crosslinking degree PSt micro-spheres

0.5 g PSt seed particles was treated with an emulsion which was prepared from 100 mL sodium dodecylsulfate (SDS) aqueous solution at 0.25% concentration and 1.56 g dibutyl phthalate by sonication. The first swelling step was carried out at 35°C for 10 h. After the first swelling step was completed, the aqueous dispersion involving the swollen particles was treated with a mixture of 4.535 g of St, 1.043 g DVB and 0.1 g BPO. Further swelling was carried out at 35°C for another 10 h. After completing the second swelling step, the resultant dispersion was added into 20 mL of polyvinyl alcohol (PVA) aqueous solution at 5% concentration. The polymerization was performed at 70°C under nitrogen for 10 h. The resulting product was treated with a centrifugal purification method and washed three times with methanol and deionized water. The mono-dispersed crosslinked PSt micro-spheres were obtained after drying under vacuum.

2 Results and discussion

2.1 The preparation of PSt micro-spheres

2.1.1 The effects of monomer concentration on the size and size distribution of the seeds

In the preparation of PSt micro-spheres process, the influence of monomer concentration on the size and size distribution of the seeds were examined. The results are listed in Table 1.

Table 1 The effects of monomer concentration on the size and size distribution of the seed particles

St/%	5	10	15	20	25	30	35	40
d/μm	1.023	1.242	1.800	2.177	2.904	3.356	4.073	4.909
ε	1.322	0.374	0.353	0.985	1.764	3.208	3.972	5.063

PVP (10%), AIBN (1%), EtOH (90 mL), H_2O (10 mL), 70°C, 10 h

It could be seen that the average particle size of the seed increases as the monomer concentration increases. The high monomer concentration at the first stage helps to increase the solubility of the resulting polymer in the reaction system which will, in turn, increase the primary polymer chain and enlarge the particle size of the seeds. When the monomer concentration was higher than 20%, the mono-dispersion index of the micro-spheres will be broaden rapidly. The second nucleation and multiple nucleation probabilities increase with increasing monomer concentration due to the formation of new particles. This will result in a broad distribution index. However, low monomer concentration will decrease the polymerization rate, prolong the nucleation and produce poor distribution primary particles. The experimental results indicate that the optimal monomer concentration is in the region of 10%–15%.

2.1.2 Effects of V (EtOH)/V (H_2O) on the size and size distribution of the seeds

It can be concluded from Table 2 that the volume ratio of ethanol and pure water influences the size and size distribution prominently for the seeds.

Table 2 The effects of V (EtOH): V (H_2O) on the size and size distribution of the seed particles

V(EtOH):V(H_2O)	100:0	95:5	90:10	85:15	80:20	75:25	70:30
d/μm	1.640	1.684	1.800	2.034	1.848	1.323	0.934
ε	0.303	0.310	0.309	0.976	2.752	4.333	5.750

St (15 mL), PVP (10%), AIBN (1%), 70°C, 10 h

The seed particle size shows an initial increase then gradual decrease. However, the distribution index exhibits a gradual increase as the amount water increases in the system. It can be proposed that PSt is insoluble in water. The critical chain length becomes short as increasing the water will favor the formation of small-sized particle micro-spheres. Meanwhile the stability of the primary nucleation particle will be affected leading to prolonged nucleation and broad particle distribution.

The SEM photographs of the seed particles [V (EtOH)/ V (H_2O) = 90:10 and 80:20] are presented in Fig. 1. The results indicate that this reaction system could be excellent when the volume ratio of V (EtOH)/V (H_2O) is between 100:0 and 90:10.

2.2 Crosslinking PSt micro-spheres by a two-step swelling method

2.2.1 Effects of different swelling reagents on the size and size distribution of the micro-spheres

The 0.5 g seed was treated with different swelling reagents at 35°C for 10 h. The size and size distribution of the micro-spheres are listed in Table 3.

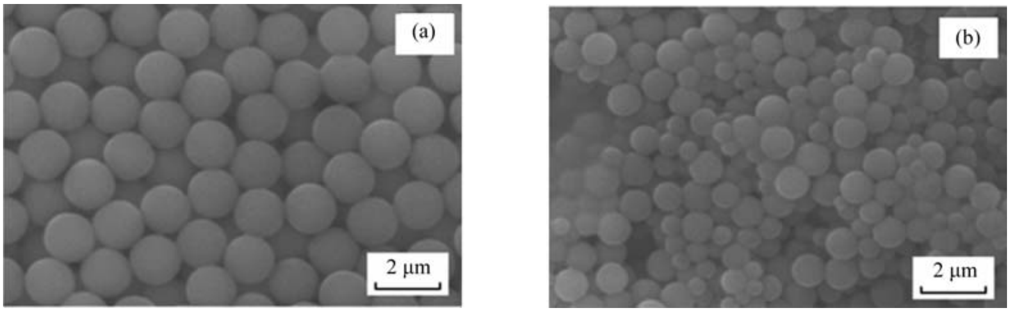

Fig. 1 The SEM photographs of the seed particles: (a) 90:10 (b) 80:20

Table 3 The effects of different swelling agents on the size and size distribution of the micro-spheres

swelling agents	toluene	*n*-heptane	*n*-octane	DBP	cyclohexane
δ	8.9	7.4	7.6	9.1	8.2
d/μm	2.96	2.98	3.01	4.56	4.63
ε	4.035	3.523	3.158	0.362	4.853

seed particles: $d = 1.80$ μm, $\varepsilon = 0.063$

The solubility parameters of St and PSt are 19.0 and 9.1, respectively [10]. Due to the similarity in their soulibilities and polarities, it can be concluded that dibutyl phalate (DBP) is a favorable solvent for PSt seeds. Poor emulsification in water of toluene, *n*-heptane *n*-octane and other similar solvents results in lower attraction of these solvent for the seed. Though cyclohexane is a good solvent for PSt seeds, seeds formed easily soften during the process and a gel will form influencing the mono-dispersed property of the seed particles drastically. Thus, DBP was selected as the swelling reagent for subsequent studies.

2.2.2 Effects of swelling reagent concentration on the size and size distributions of micro-spheres

Figure 2 shows the effect of the swelling reagent concentration on the size and size distributions of micro-spheres with DBP as the swelling reagent.

It can be seen that the average particle size of the micro-spheres and their distribution index increase gradually as DBP concentration increases. The increasing DBP concentration will help DBP diffuse into the seeds and favor the formation of large-sized particles. When the concentration is higher than 32%, DBP will form little drops which will compete with seeds and result in a broad size distribution.

The particle size distribution examined by PSA is shown in Fig. 3. When the content of DBP is 30%, the particle size is uniform and the index is low but when the value is increased to 50%, the particle size is completely different. The results indicate that when the DBP is between 20% and 30%, the mono-dispersed property of the micro-spheres is good.

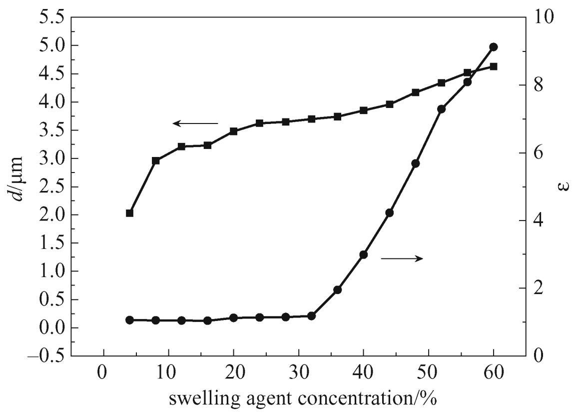

Fig. 2 The effects of swelling agent concentration on the size and size distributions of the micro-spheres (seed particles: $d = 1.80$ μm, $\varepsilon = 0.063$)

2.2.3 Effects of DVB concentration on the size and size distribution of the micro-spheres

It can be seen from Table 4 that low crosslinking reagent concentration will produce good mono-dispersed and small size micro-spheres. The mono-dispersed index and size of the micro-spheres increase with increasing DVB concentration. When the DVB concentration is higher than 25%, a lot of free detached droplets will form which will result in non-sphere particles influencing the mono-dispersed property severely. The experimental results show that the favorable DVB concentration is 23%.

2.2.4 Effects of swelling temperatures on the size and size distribution of the micro-spheres

The influences of swelling temperature on the results of size and size distribution for the micro-spheres are listed in Table 5.

The average particle size and the distribution gradually increase as the swelling temperature increases. High temperature favors diffusion of the swelling reagent which will lead to larger particle size. However, when the swelling temperature is higher than

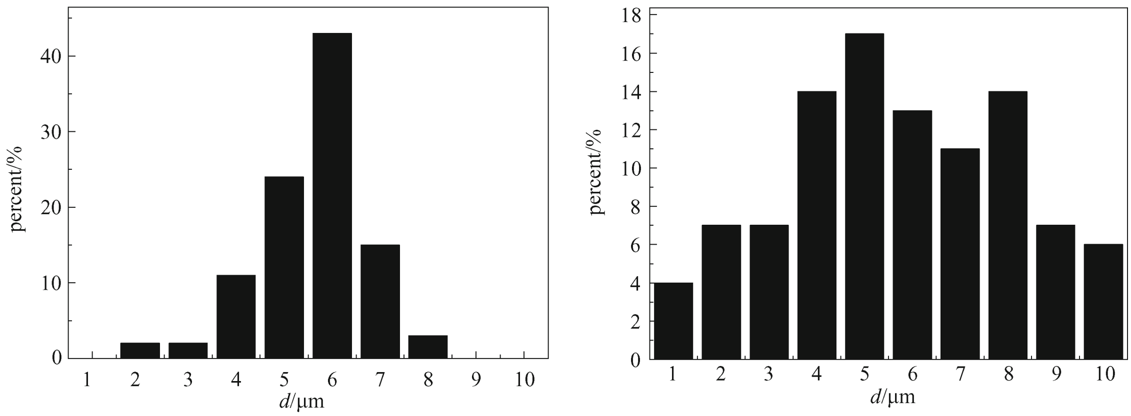

Fig. 3 The effects of DBP concentration on the size distributions of the micro-spheres: A) 30% DBP; B) 50% DBP (seed particles: $d = 1.80$ μm, $\varepsilon = 0.063$)

Table 4 The effects of DVB concentration on the size and size distributions on the micro-spheres

DVB/%	5	10	15	20	25	30
d/μm	5.085	5.942	6.043	6.748	7.328	8.094
ε	0.074	0.071	0.072	0.305	3.354	4.028

seed particles: $d = 1.80$ μm, $\varepsilon = 0.063$

Table 5 The effects of swelling temperatures on the size and size distribution of the micro-spheres

T/°C	20	25	30	35	40	45	50
d/μm	6.43	6.85	7.03	7.10	7.25	7.28	7.39
ε	0.138	0.142	0.147	0.147	0.379	1.332	2.796

seed particles: $d = 1.80$ μm, $\varepsilon = 0.063$

40°C, the gelatin action will emerge and the mono-dispersed property will be affected severely. The SEM photographs of the micro-spheres which were obtained at the swelling temperature of 30°C and 45°C are shown in Fig. 4. It can be seen that the morphology of the micro-spheres at 30°C is better than that at 45°C. The mono-dispersed property is excellent. The experimental results indicate that the optical swelling temperature is between 20 and 35°C.

2.2.5 Effects of different stirring speeds on the size and size distribution of the micro-spheres

The effects of stirring speeds on the size and size distribution of the micro-spheres are listed in Table 6.

It can be seen that the average particle size decreases gradually as the stirring speed increases. However, the distribution index exhibits an initial increase then followed by a decrease. When the stirring speeds were too low, the monomer could not be diffused completely and the distribution becomes broad. When the stirring speed is increased, the diffusion of the monomer is enhanced and the micro-sphere's distribution will be improved. However, when the stirring speed is higher than 220 r/min, the swelling micro-spheres will be destroyed by the stirring effect and the distribution will become broader. The experimental results indicate that the favorable stirring speeds are between 140 and180 r/m.

2.2.6 The DSC analysis of the PSt micro-spheres

The DSC analysis results of the PSt micro-spheres were described in Fig. 5. The glass transition temperature of the PSt seed before crosslinking is 98°C. The crosslinking

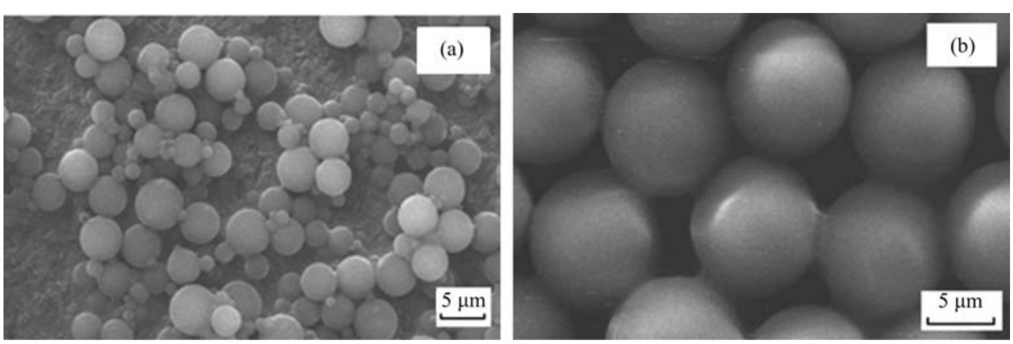

Fig. 4 The SEM photographs of micro-spheres with different swelling temperatures: A. 45°C; B. 30°C (Seed particles: $d = 1.80$ μm, $\varepsilon = 0.063$)

Table 6 The effects of different stirring speeds on the size and size distribution of micro-spheres

stirring speed /r·min^{-1}	60	100	140	180	220	260	300
d/μm	13.24	9.03	7.10	6.54	5.32	3.78	2.95
ε	3.273	0.954	0.107	0.370	1.385	1.452	2.033

seed particles: $d = 1.80$ μm, $\varepsilon = 0.103$

network structure was formed after the addition of DVB and a seed swelling polymerization process. The glass transition temperature of this crosslinked structure reaches 125°C. The thermal resistance of the PSt micro-spheres was evidently improved.

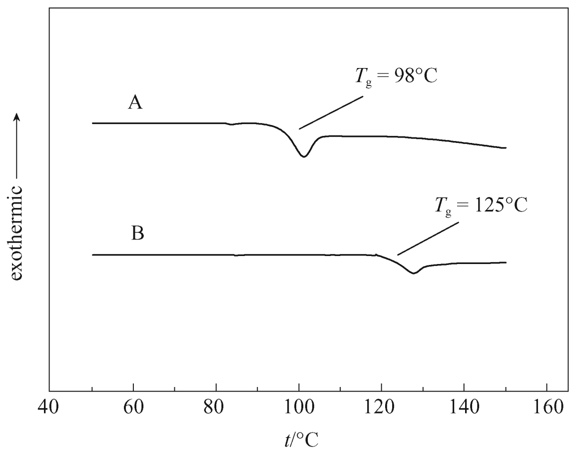

Fig. 5 DSC result for polymer micro-spheres
A) PSt micro-spheres; B) Micro-spheres after swelling

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