

Preparation of highly cross-linked monodispersed functional polystyrene particles by utilizing the delayed addition method

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Abstract A facile and effective method was successfully developed to prepare the highly cross-linked monodispersed PS particles via soap-free emulsion polymerization, in which the cross-linking agent (DVB) was delayed addition by varying time (Delayed Addition Method, DAM). Through this method, the highly cross-linked monodispersed particles with functional groups on its surface can be prepared. The particles prepared by DAM had a uniform size distribution for the St/DVB and St/HEMA/DVB system. For the St/DVB system, when the cross-linking agent (DVB) was added delay 3 or 7 h, cross-linked PS particles could be successfully prepared without a significant change in the narrow particle size distribution even containing up to 40 wt% of DVB. Similarly, for the St/HEMA/DVB system, by delayed addition of DVB for 3 h, stable and monodispersed polymer particles still could be prepared even the containing of DVB reach to 60 wt%. Moreover, when the feed composition of the DVB kept constant, the longer the delayed addition time of DVB, the better the monodispersity of the cross-linked particles were.

Introduction

For a long time, polymer colloids have been used in a wide range of practical applications and advanced material fields, such as in water-borne coatings and adhesives,

information technology, electric and electronic device, and biochemical and biomedical applications [1–4]. In order to fulfill their applications, precise control of the morphology and structures of the polymer particles becomes more important, such as the particle size and size distribution, morphology, functionality, and degree of crosslinking of the polymer beads. To date, stable and functional polymeric particles with highly cross-linked structure have received much attention because of their extensive application in various fields [5, 6], including protein synthesis and biomedical applications [7, 8]. Therefore, the development of a facile technique to synthesize monodispersed polymer particles with different cross-linked degree becomes an important object.

Just as we have known, dispersion polymerization is an important method to prepare monodispersed micro-size polymer particles. However, when the functional comonomers were employed in the dispersion polymerization, some problems [9–11] have encountered, including loss of control of particle size, broadening of the size distribution, odd-shaped particles, and coagulation of the polymer produced in the reaction. Another biggest challenge for dispersion polymerization is synthesis of cross-linked particles. There are many papers [12–14] to state that dispersion polymerization failed when cross-linking agents are present. Even if the reaction appears to succeed, the particles with odd-shaped and broad size distribution were usually obtained [15, 16]. Therefore, preparation of highly cross-linked and monodisperse micro-size polymer particles puzzled people for a long time. Recently, Winnik et al. [17, 18] discovered that micron-size cross-linked particles with narrow size distribution could be obtained by delayed addition of cross-linking agent after the end of the nucleation stage in the dispersion polymerization. Winnik's method well dissolved the problem to preparation of highly

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cross-linked monodispersed polymer particles with micron size, but for highly cross-linked monodispersed polymer particles with sub-micron size, it is still a big problem and no more papers carefully dealt with this problem.

Herein, we first used the delayed addition of the cross-linking agent in soap-free emulsion polymerization to prepare the highly cross-linked monodisperse polystyrene particles with sub-micron size, which is composed of various concentrations of divinylbenzene from 5 to 60 wt% based on styrene monomer. Moreover, functional comonomer, 2-hydroxyethyl methacrylate (HEMA), has been copolymerized into the monodisperse particles and highly cross-linked polystyrene particles with hydroxyl group on its surface were obtained. Some influencing parameters, such as the added time and concentration of the cross-linking agent on the stability and monodispersity of the particles, were investigated in detail.

Experimental

Materials

Styrene (St) was purchased from Shanghai Chemical Reagent Co. (China), and was distilled under reduced pressure before use. Divinylbenzene (DVB-55), containing 55% of the para- and meta-divinyl isomers and 45% of the para- and meta-ethyl vinyl isomers, and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich Chemical Co., all of them were purified with a basic alumina column. Potassium persulfate (KPS) was purchased from the Shanghai Aijian Reactant Factory (China) and was used without further purification. Water was distilled and deionized (DDI) by employing a Milli-Q water purification system. The other reagents and solvents were used as received without any further treatment.

Preparation of cross-linked polystyrene particles by batch process

The soap-free emulsion polymerization was conducted by a batch process, which was performed in a 250-mL, four-necked, round-bottom flask equipped with a polytetrafluoroethylene-bladed paddle stirrer, a water-cooled reflux condenser, an argon inlet, and a thermometer. The typical procedure is as follows: the monomer, including styrene and DVB, and water were added, argon was passed through the water in the flask for 30 min under 200 rpm agitation, and then the temperature was elevated. When the temperature reached 70 °C, the KPS (0.12 g) in aqueous solution was injected using a syringe to initiate polymerization, and the polymerization was performed at 70 °C for 24 h.

Preparation of cross-linked polystyrene particles by delayed addition of DVB

The recipe and procedure were similar to that described above, except that the DVB was added after the start of the polymerization for 3 or 7 h.

Preparation of cross-linked poly(St/HEMA) composite particles by batch process

The soap-free emulsion polymerization was performed in a 250-mL, four-necked, round-bottom flask equipped with a polytetrafluoroethylene-bladed paddle stirrer, a water-cooled reflux condenser, an argon inlet, and a thermometer. Typically, the monomer, including styrene, HEMA (20 wt% based on styrene) and DVB, and water were charged into the flask, argon was passed through the solution in the flask for 30 min under 200 rpm agitation, and then the temperature was elevated. When the temperature reached 70 °C, the KPS (0.12 g) in aqueous solution was injected using a syringe to initiate polymerization, and the polymerization was performed at 70 °C for 24 h.

Preparation of cross-linked poly(St/HEMA) composite particles by delayed addition of DVB

The recipe and procedure were similar to that described above, except that the DVB was added after the start of the polymerization for 3 h.

Characterization

The average particle size was determined by dynamic light scattering (DLS) performed on a Malvern Autosizer 4700, and the laser wavelength (λ) applied in the measurements was 514.5 nm. All measurements were carried out at 25 °C at a fixed angle of 90°, and the measured particle sizes were Z-averaged diameters. SEM images were recorded on a scanning electron microscope (SEM Philips XL30 apparatus). The composite particles dispersions were diluted, dried on a cover glass, and sputter-coated with gold prior to observation.

Results and discussion

Preparation of cross-linked polystyrene particles by batch process

A series of DVB cross-linked PS particles were synthesized via the soap-free emulsion polymerization, the feed

composition and particle size are summarized in Table 1. From Table 1, we can see that stable latex could be prepared under our experimental conditions with lower 20 wt% DVB in the feed composition. However, with a higher DVB content (40 wt%), flocculation occurred after only 10 min initiation, and the aggregates severely emerged during the polymerization, finally, a unstable latex was obtained. As shown in Table 1, average particle sizes slightly went down with increase of the feed composition of DVB. SEM images of the cross-linked particles are presented in Fig. 1. Without the cross-linking agent, just as we know, the PS particles are monodisperse (Fig. 1a). When 5 wt% DVB was added to the system, the PS particles are still kept monodisperse as shown in Fig. 1b. However, when DVB is increased to 20 wt%, as shown in Fig. 1c, the cross-linked PS particles become polydisperse. These results suggest that if the cross-linking agent was added in a batch mode, the amount of the cross-linking agent must be well adjusted if one wants to maintain a narrow size distribution. These results are similar to that has been reported by Zou et al. [19]. As shown in Table 1, the average diameter of the polystyrene particles went down with increase of DVB content. According to the references [17, 18], DVB is more reactive, which leads to rapid depletion of DVB in batch emulsion copolymerization. With increasing the amount of DVB, the nucleation

Table 1 Recipes and particle size of PS emulsion by batch process^a

Runs	St (g)	DVB		D (nm) ^c
		(wt%) ^b	(g)	
A1	3.00	0	0	450
A2	2.85	5	0.15	420
A3	2.40	20	0.60	300
A4	1.80	40	1.20	Coagulation

^a The recipes included 0.12 g KPS and 100 g deionized water and the reaction temperature is 70 °C

^b Based on the total monomer

^c Average particle diameter determined by DLS

locus of the primary particles increased and the number of particles increased as well due to the rapid nucleation of DVB, and the final diameter of the polystyrene particles should decrease.

Preparation of cross-linked polystyrene particles by delayed addition of DVB

To avoid the influence of higher amount of DVB on the nucleation stage of cross-linked PS particles, we delayed the addition of DVB until 3 or 7 h after the initiation of the polymerization, respectively. The recipes and particle size are presented in Table 2. From Table 2, the stable cross-linked PS particles cannot be obtained when the concentrations of DVB is more than 60 wt%, this means that the permitted maximal levels of DVB are 60 wt% in this reaction system.

Table 2 Recipes and particle size of polystyrene composite particles obtained by the delayed addition method^a

Runs	Time of addition DVB (h)	St (g)	DVB		D (nm) ^c
			(wt%) ^b	(g)	
B1	3	2.70	10	0.30	430
B2	3	2.40	20	0.60	460
B3	3	2.10	30	0.90	470
B4	3	1.80	40	1.20	430
B5	3	1.20	60	1.80	420
B6	3	0.60	80	2.40	Coagulation
C1	7	2.40	20	0.60	490
C2	7	1.80	40	1.20	380
C3	7	1.20	60	1.80	380
C4	7	0.60	80	2.40	Coagulation

^a The recipes included 0.12 g KPS and 100 g deionized water and the reaction temperature is 70 °C

^b Based on the total monomer

^c Average particle diameter determined by DLS

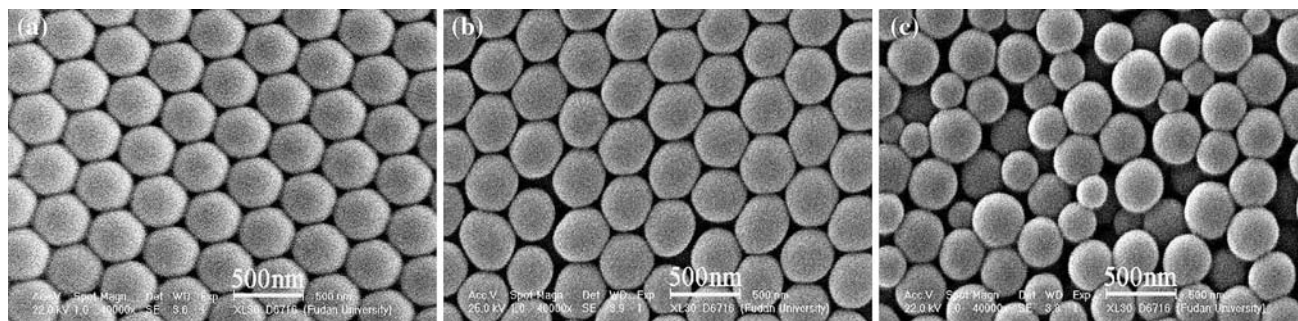


Fig. 1 SEM images of polystyrene particles by batch process: (a) A1; (b) A2; (c) A3. (Scale bar is 500 nm)

Fig. 2 SEM images of polystyrene particles obtained by the delayed addition of DVB: (a) B1; (b) B2; (c) B3; (d) B4; (e) B5; (f) C1; (g) C2; (h) C3. (Scale bar is 500 nm)

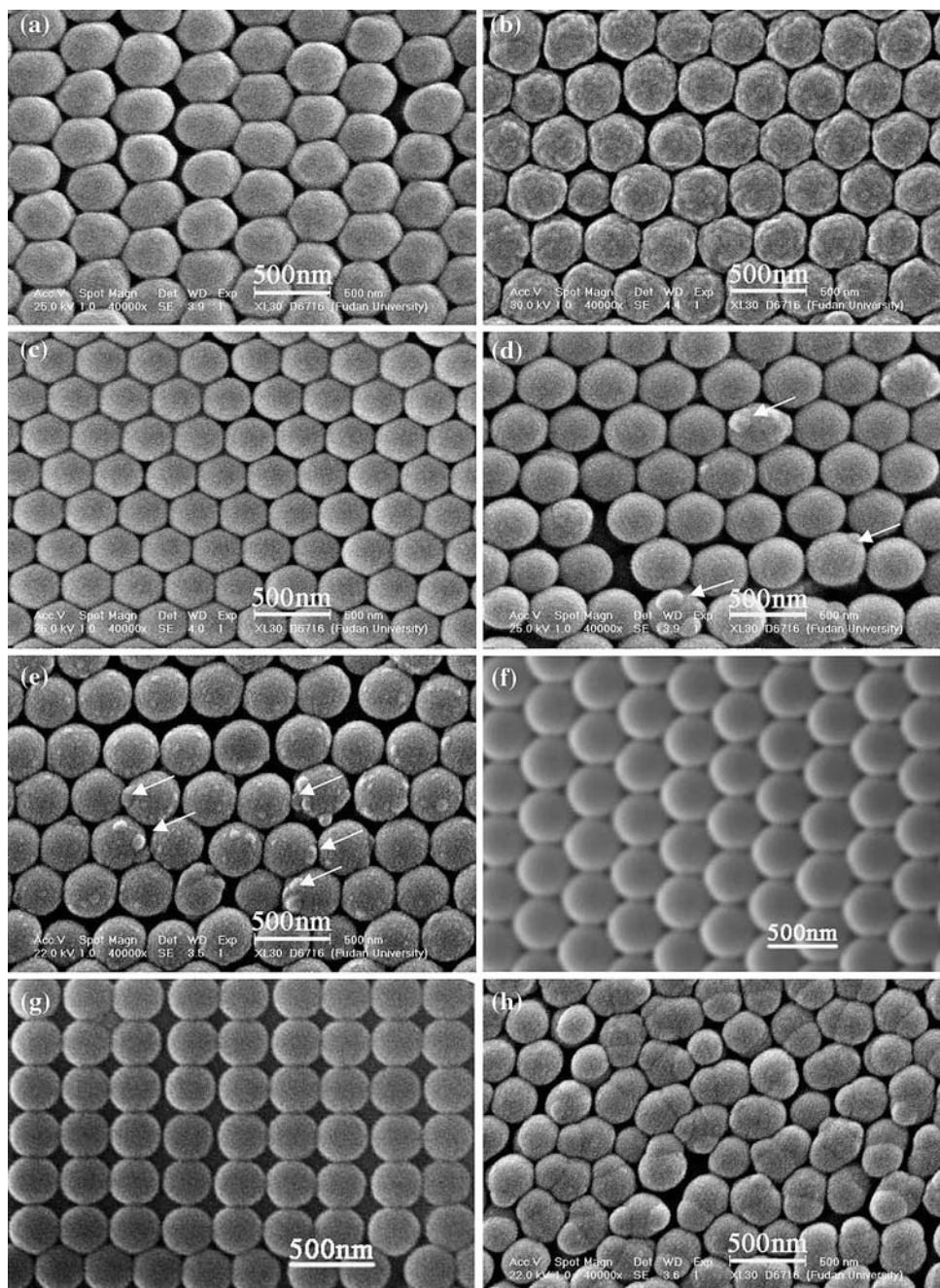


Figure 2 displayed some representative SEM images of the cross-linked particles that obtained by the delayed addition of DVB. When the concentration of DVB is varied from 10 to 30 wt%, the PS particles kept rather narrow size distribution (Fig. 2a–c), except that the surface of the particle (runs B2 in Table 2) is not very smooth (Fig. 2b). This suggests that the cross-linked density of the particles and maintaining their very narrow size distribution could be improve by delayed addition of cross-linking agent compared with Fig. 1c. Increased the DVB to 40 wt%, as a whole, the PS particles are still monodisperse (Fig. 2d), but, some of the PS particles have tiny rough features on

the surface (see arrows in TEM image). When 60 wt% DVB was added to the system, the more tiny rough features emerge on the surface of the particles which is no longer smooth, as shown in Fig. 2e. Through the delayed addition of DVB for 3 h, it is obvious that the cross-linked density of the PS particles was improved prominently and the size distribution of the PS particles was still very narrow. All this was attributed to the effective avoidance of the secondary nucleation by the delayed addition method [17, 18].

During the delayed addition of DVB for 7 h, a much longer delayed time, SEM images of the cross-linked particles were also obtained (Fig. 2f–h). The recipes are

Table 3 Recipes and particle size of poly(St/HEMA) composite particles by batch process^a

Runs	St (g)	HEMA ^b (g)	DVB		D (nm) ^d
			(wt%) ^c	(g)	
D1	2.40	0.60	0	0	250
D2	2.16	0.54	10	0.30	310
D3	1.92	0.48	20	0.60	310
D4	1.44	0.36	40	1.20	330
D5	0.96	0.24	60	1.80	Coagulation

^a The recipes included 0.12 g KPS and 100 g deionized water and the reaction temperature is 70 °C

^b wt(HEMA):wt(St) = 1:4

^c Based on the total monomer

^d Average particle diameter determined by DLS

presented in Table 2 (C1–C4), the cross-linked PS particles could well keep narrow particle size distribution before 40 wt% DVB containing (see Fig. 2f and g). None of the tiny rough features emerge on the surface of polymer particles, which suggests that the secondary nucleation of the particles obtained by the delayed addition of DVB for 7 h is negligible. When DVB increased to 60 wt%, the obtained PS particles were still stable, but, interestingly, the cross-linked PS particles have irregular shapes, as shown in Fig. 2h, the detail reason is not clear now. When DVB content is lower than 40 wt%, the seed polystyrene particles is more stable due to the smaller surface area and the enough sulfate groups anchored on the surface. As a result, a stable polystyrene latex could be obtained after the polymerization. Increasing DVB content to 60 wt%, the secondary nucleation was emerged (Fig. 2e and h), and

Table 4 Recipes and particles size of poly(St/HEMA) composite particles by the delayed addition of DVB for 3h^a

Runs	St (g)	HEMA ^b (g)	DVB		D (nm) ^d
			(wt%) ^c	(g)	
E1	2.16	0.54	10	0.30	250
E2	1.92	0.48	20	0.60	250
E3	1.68	0.42	30	0.90	270
E4	1.44	0.36	40	1.20	240
E5	0.96	0.24	60	1.80	290
E6	0.48	0.12	80	2.40	Coagulation

^a The recipes included 0.12 g KPS and 100 g deionized water and the reaction temperature is 70 °C

^b wt(HEMA):wt(St) = 1:4

^c Based on the total monomer

^d Average particle diameter determined by DLS

further increase to 80 wt%, the stability of the latex has been broken by the heavy secondary nucleation.

Figures 1c, 2b and f were the cross-linked PS particles with 20 wt% DVB, which were prepared by batch addition of DVB, 3h and 7h delayed addition of DVB, respectively. The particles prepared by the delayed addition method were monodisperse, while the particles prepared by batch method were polydisperse. Similarly, as for the particles containing 40 wt% DVB, the latexes obtained by the batch addition method were unstable, whereas the particles obtained by the delayed addition of DVB for 3 and 7 h were stable and monodisperse. This suggests that the stability and monodispersity of the particles prepared by the delayed addition method was prominently improved under same average cross-linked density. Moreover, the

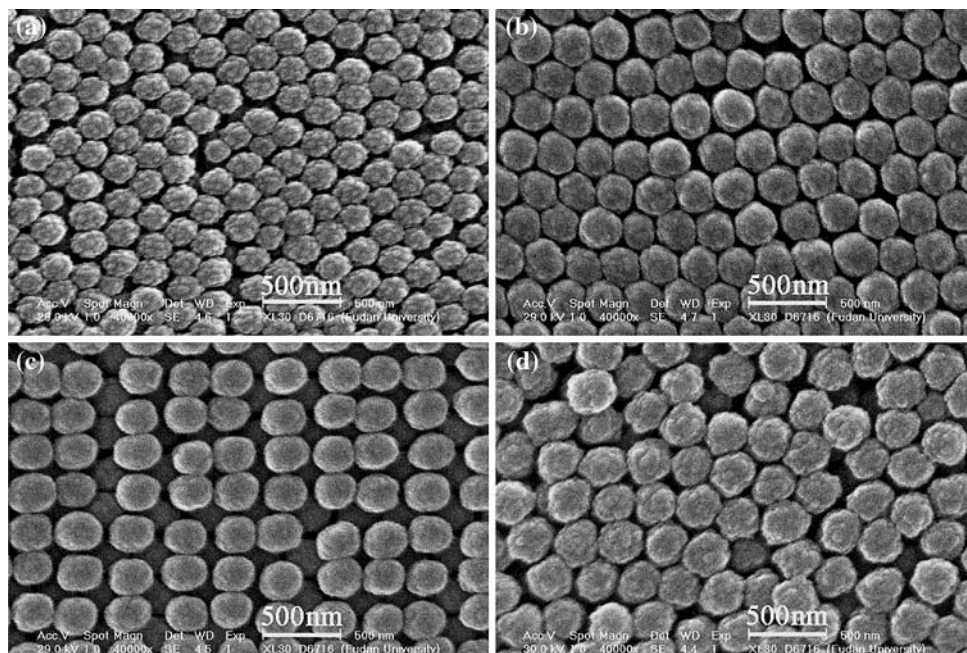
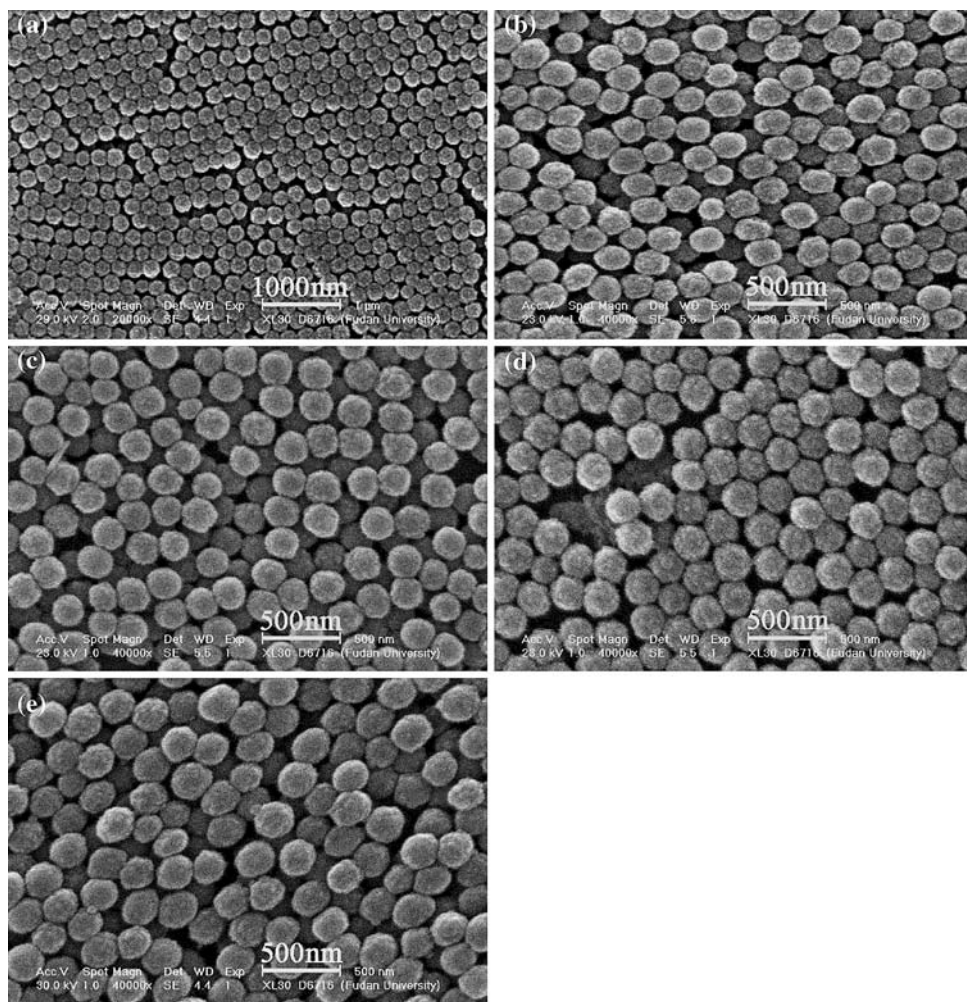
Fig. 3 SEM images of poly(St/HEMA) composite particles by the batch process: (a) D1; (b) D2; (c) D3; (d) D4. (Scale bar is 500 nm)

Fig. 4 SEM images of poly(St/HEMA) composite particles obtained by the delayed addition of DVB for 3 h: (a) E1; (b) E2; (c) E3; (d) E4; (e) E5. (Scale bar is 1,000 nm in a and 500 nm in b, c, d, e)



concentration and time span of the delayed addition of DVB are the crucial factors in determining final structures and performance of the cross-linked particles. That is, as for the same composition of the DVB, the longer the delayed time of the addition of DVB, the less were the influence on the size distribution and colloid stability of the cross-linked particles. In this way, the monodisperse and highly cross-linked PS particles can be obtained in the soap-free emulsion polymerization. Similar results were also obtained for 60 wt% DVB system.

Preparation of cross-linked poly(St/HEMA) composite particles by batch process

In order to obtain highly cross-linked monodispersed PS particles with functional group on its surface, functional comonomer, 2-hydroxyethyl methacrylate (HEMA), has been copolymerized into the reaction system. HEMA is one of the widely used hydrophilic monomers carrying the hydroxyl functionality. The typical recipes are presented in

Table 3. Obviously, the average particle sizes of the St/HEMA/DVB system is smaller than the St/DVB system. This probable reason should relate to the hydrophilicity of the monomer HEMA. Due to the hydrophilicity of the functional monomer (HEMA), the concentration of monomer in aqueous phase is high at the early stage of nucleation, which could result in a large number of primary particles [20–22]. Besides, the hydrophilic oligomer of HEMA anchored onto the surface of particles could enhance the stability of the primary particles [22]. All these factors should lead to small size particles. Figure 3a presented the SEM image of Poly(St/HEMA) particles without DVB. From the image, we could see some raspberry-like particles had obtained, these results are consistent with the report of Kamei et al. [21]. In our reaction system, when DVB content is more than 40 wt%, the latexes become unstable. In this system, the stability of the particles copolymerized with HEMA is higher than the particles without HEMA. This is probably because that the stability of the particles was improved due to the copolymerization of the hydrophilic HEMA.

With increase of the feed amount of DVB, the surface of the particles gradually becomes smooth (Fig. 3b and c). Further increase of DVB will result new phase separation and the surface of the particles become uneven again (Fig. 3d).

Preparation of cross-linked poly(St/HEMA) composite particles by delayed addition of DVB

Table 4 shows the recipe of the poly(St/HEMA/DVB) composite particles prepared by the delayed addition of DVB for 3 h. The process is similar to above section (in Table 3) except for the addition time of DVB. The feed amount of DVB is various from 10 to 60 wt%. In batch method, the maximal feed amount of DVB to prepare stable poly(St/HEMA) composite latex is 40 wt%. However, in the delayed addition method, when the feed amount of DVB was increased to 60 wt%, the size distribution of the particles still maintains uniform, and the surface is also better than the batch process (Fig. 4a–e).

Conclusions

A novel and facile method, in which the cross-linking agent (DVB) was delayed addition for varying hours, was successfully conducted to prepare the highly cross-linked monodisperse PS composite particles via soap-free emulsion polymerization. Moreover, highly cross-linked PS composite particles with functional hydrophilic group on its surface were obtained; these particles prepared by the delayed addition method possessed uniform size distribution. For the St/DVB system, in batch process, 20 wt% feed amount of DVB (based on the total monomer) in the reaction system resulted in broaden particle size distribution and 40 wt% feed amount of DVB led to coagulation. Whereas, when the cross-linking agent (DVB) was delayed addition for 3 or 7 h, the cross-linked monodispersed PS particles containing up to 60 wt% of DVB could be obtained without a significant change in the narrow particle size distribution. Similarly, for the St/HEMA/DVB system, by the delayed addition of DVB for 3 h, the concentration of DVB can be enhanced from 40 to 60 wt% and the particles still maintain monodisperse. In our experiment, we also found that the longer the delayed time of DVB addition, the better were the monodispersity of the

cross-linked particles. Based on this study, it could be believed that the monodisperse and highly cross-linked particles with functional group on its surface can be conveniently prepared by the delayed addition method.

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