Front. Chem. China 2007, 2(1): 17–20
DOI 10.1007/s11458-007-0004-x

RESEARCH ARTICLE

LIU Kaiyi, WANG Zhaoqun

A novel method for preparing monodispersed polystyrene nanoparticles

Abstract A preparation manner for monodispersed polystyrene (PS) nanoparticles polymerized by using a novel addition procedure of a monomer is suggested. In systems containing a smaller amount of surfactant compared with conventional microemulsion polymerization, the polymerization processes consists of three stages: adding dropwise the first part of the monomer for a few minutes at 80°C and polymerizing for 1 h; adding collectively the residual part of the monomer and polymerizing at the same temperature for another 1 h; and then polymerizing at 85°C for another 1 h. Based on discussions on the nucleation mechanism of particles in the polymerization system, the influences of monomer weight added dropwise, and amounts of initiator and emulsifier on the size and distribution of PS particles were investigated. PS nanoparticles with smaller diameter such as a number-average diameter of 18.7 nm and better monodispersity were obtained since the dropped styrene amount was suitable under 20wt-% emulsifier amount and 3wt-% initiator amount based on the monomer.

Keywords polystyrene, nanoparticle, monodispersity, microemulsion polymerization, monomer-added procedure

1 Introduction

Polymer nanomaterials have potential application in a wide field such as high performance coatings, electric materials, catalysts, drug delivery carriers, and biomedical materials, etc. Therefore, the studies on their synthesis and size control have been receiving a great amount of attention in recent years. Monodispersed polymer nanoparticles with a diameter larger than 50 nm can be synthesized by conventional emulsion polymerization. Further reduction in particle size can be achieved by microemulsion polymerization. However, the drawbacks of the microemulsion method are well-known, including the requirement of a much larger number of surfactant (surfactant/monomer weight ratio >1, usually) and only a relatively low polymer content (<10wt%, usually) in the produced latex besides wider diameter distribution of the resulting particles.

On the other hand, as a widely applied polymer material and an important model system for theory research, the synthesis of polystyrene (PS) nanoparticles and their size control have attracted great attention [1–4]. Ming and Fu et al. [5] have synthesized PS nanoparticles with a weight-average diameter (D_w) of 21.6 nm by dropping styrene (St) into a microemulsion system using sodium dodecyl sulfate (SDS) as surfactant, but the SDS/St weight ratio was as large as 7.4. Subsequently, Ming et al. [6] have reported a modified microemulsion polymerization method, in which a small amount of monomer was first added into the reaction system, and then the residual monomer was added dropwise. At an SDS/St weight ratio of 0.15, the number-average diameter (D_n) and the D_v (viscosity-average diameter)/D_n were 15.3 nm and 1.52, respectively in the initial stage of the reaction, but at the end of the polymerization, the D_n and D_v was increased to about 32 nm and 37 nm, respectively. Zhang et al. [7] have prepared PS nanoparticles with D_n of 30 nm and a good monodispersity ($D_w/D_n = 1.06$) by an ultrasonically induced microemulsion polymerization. However, the weight ratio of both surfactant/St and auxiliary surfactant 1-pentanol/St reached to about 1.0 and particularly, the monomer conversion was only 70%. Xu et al. [8] have synthesized PS nanoparticles by a procedure of adding a monomer similar to Ref. [6] in a microemulsion polymerization system with a redox initiator and used cetyltrimethylammonium bromide as surfactant. Though a small amount of surfactants (7% of St weight) was used, the resulting D_w was as large as 46.1 nm. As the surfactant/St weight ratio was increased to 0.30, the D_w of PS particles decreased to 37.6 nm and there was no marked effect on decreasing particle size. Recently, He et al. [9] have studied the preparation of PS nanoparticles by a particular seeded polymerization. The polymerization was started with a small amount of methyl methacrylate (MMA) to form dynamic

Translated from *Journal of Nanjing University* (*Natural Science*), 2006, 2 (in Chinese)

LIU Kaiyi, WANG Zhaoqun (✉)
Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
E-mail: zqwang@nju.edu.cn

nanoseeds, and then St was added in a differential manner for about 1.5 hrs. The resulting PMMA/PS nanoparticles with a z-average diameter (D_z) smaller than 20 nm were obtained at an SDS/ (MMA + St) weight ratio of 0.043, whereas the D_z of PS particles was 23.3 nm without MMA added in the beginning and the SDS/St weight ratio reached 0.26.

Apparently, the PS nanoparticles are still restricted in further size reduction by the requirements of surfactant content. Besides, the relatively wider size distribution of the PS nanoparticles prepared by most methods mentioned above should receive merited attention. In this paper, a novel addition method of the monomer is suggested, by which studies on preparing PS nanoparticles with much smaller diameter and also good monodispersibility are carried out in a microemulsion polymerization system containing a small amount of surfactant.

2 Experimental

2.1 Materials

Styrene (St) from Shanghai Chemical Reagent Co., Ltd. was purified by washing, drying, and then distillation under reduced pressure before use. Potassium persulfate (KPS) and sodium dodecylsulfate (SDS) of analytical reagent grade (Jiangsu Huakang Chemical Co.) was purified by recrystallization in water. 1-Butanol of analytical reagent grade (Shanghai Chemical Reagent Co., Ltd.) was used as received. Distilled water was employed as polymerization medium and in other experiments.

2.2 Synthesis of monodispersed PS nanoparticles

The addition process of St was divided into two stages: stage 1, slowly dropping first a part of the monomer (St_1) into a polymerization system and stage 2, adding the residual monomer (St_2) in one batch. A typical polymerization procedure is described as follows. SDS dissolved in water of 90 mL was added in a 250 mL four-necked flask equipped with a reflux condenser, mechanical stirrer and nitrogen inlet. Then, KPS dissolved in 10 mL water was added after raising the temperature to 80°C. Under mild mechanical stirring at about 200 rpm, the mixture of St_1 and 1-butanol was slowly dropped into the system for about 30 min and prolonged stage 1 to 1 h. Then, St_2 was added all together into the flask and leave the reaction for another 1 h. Finally, the polymerization temperature was raised to 85°C and continued for another hour before cooling the reactor to room temperature.

2.3 Analysis

Particle size and size distribution of the PS were determined by dynamic light scattering method with a 90PLUS Particle Analyzer (Brookhaven Instruments Co.) at room temperature, before which the PS latexes were diluted with water to a solid content of about 0.1wt%. The number-average diameter (D_n), weight-average diameter (D_w) and monodispersity index expressed as D_w/D_n were obtained directly from the measurement results. The morphology of the PS particles was observed with transmission electron microscopy (TEM, JEM-100S, JEOL).

3 Results and discussion

3.1 Influence of monomer amount in stage 1

In the early polymerization period, a relatively higher weight ratio of the surfactant and monomer was made effectively by dividing the monomer addition into two stages. Moreover, the monomer added in stage 1 (St_1) was slowly dropped into the system, which further increased the instantaneous concentration of the surfactant relative to the monomer and maintained the system at a monomer-starved state for a long period of time. Once added into the system, the monomer would either diffuse rapidly to dissolve into a water phase, enter the micelles or form a number of tiny droplets. The monomer, whether existing as micelles, water phase or tiny drops, would catch free radicals and be initiated to start the polymerization. Therefore, it is possible for multiform nucleation to occur simultaneously in stage 1, including micelle nucleation, homogeneous nucleation owing to precipitation of St oligomeric radicals adsorbing emulsifier in water, and "tiny droplet nucleation". The homogeneous nucleation should not be ignored anymore compared with a conventional emulsion polymerization because the consumed amount of the monomer converted to polymer in all units is usually proportional to the slow supply of monomer added in small droplets. Furthermore, a large number of surfactant is not required for the stability of the monomer in a starved state. It is reasonable to imagine that the nucleation in the system is controlled obviously by the monomer amount and its manner of addition. In other words, the monomer and surfactant in the system should be used furthest to form more amounts of particle nucleus in stage 1.

If the above argument is logical, the nuclear number and final particle size would be distinctly influenced by the monomer weight added in stage 1. Table 1 shows the results of average diameter and monodispersity of PS particles

Table 1 The average diameter and monodispersity index of PS nanoparticles prepared in polymerization systems[a] with different W_{s1}

Sample No.	W_{s1}[b] (g)	W_{s2}[b] (g)	D_n (nm)	D_w (nm)	D_w/D_n	C[c] (%)
509C	1.00	4.00	23.6	24.3	1.03	99.5
510B	1.50	3.50	18.7	20.4	1.09	94.2
511A	2.00	3.00	21.7	22.4	1.04	90.8
511C	3.00	2.00	20.6	21.2	1.03	91.5
507[d]	5.00	0.00	22.3	24.2	1.09	86.6

a. Water, 100 mL; KPS, 0.15 g; n-Butanol, 0.10 g; SDS/St, 1/5 (g /g);
b. With a constant total weight of St ($W_s = W_{s1} + W_{s2}$), 5 g;
c. Monomer conversion ratio;
d. KPS, 0.05 g; dropping monomer for 2 h.

obtained at different St_1 weight (W_{s1}) while the total amount of the monomer (W_s) is kept constant. The influence of W_{s1} on the diameter of PS particles and its trend were distinctly observed in Fig. 1, in which the size of the PS particles decreased with increase of W_{s1} at beginning and reached the smallest size of 18.7 nm as W_{s1} was 1.5 times the SDS weight (W_e). When W_{s1} was equal to the total weight of the monomer, that is when the entire monomer was all dropped into the reacting system, the average diameter of the PS particles rose slightly. Noticeably, their diameter distribution became wide and another peak appeared at 50 nm as shown in Fig. 2. This suggests that dropping the styrene at the extreme or total amount should bring on a more complicated nucleation procedure similar to continual nucleation in conventional microemulsion polymerization [10], which gives the polymerizing units an unfair chance to gain the monomer. It can be concluded that St_1 has a more appropriate amount dependent on the used SDS amount to decrease the size and improve monodispersity of the particles, not always the most amount or all of the monomer.

3.2 Influence of initiator amount

Converting the latent possibility of plentiful nucleation into a reality depends on a sufficient amount of radicals, which is made possible by proper proportions of monomer and surfactant in stage 1. A higher polymerization temperature of 80°C was chosen to accelerate the thermodecomposition of the KPS and form simultaneously a large number of free radicals. Besides, aqueous solubility of St can be increased to intensify the effect of homogeneous nucleation. Nevertheless, KPS amount is an important and direct factor that influences nucleation and the resulting particle size. Table 2 shows the influence of KPS weight (W_i) on the size and monodispersity of PS particles. It can be found that the monodispersity index (D_w/D_n) of the PS particles prepared by using more W_i was good, whereas the diameter distribution became wider when a lower W_i was added. A double-peak for weight intensity appeared in the diameter spectrum as KPS content of 1% based on monomer weight was used in sample 511B, and there was an accumulative weight fraction of 24% for the second peak larger than that of sample 507 shown in Table 1. This suggests that more nucleuses should form in a short time with sufficient radicals and contrarily, the nucleation period should be prolonged even to the end of the reaction process at a lower KPS content, which leads to a bad monodispersity. It is because of the lower conversion ratio of the monomer that sample 511B showed an abnormality in the diameter. If considering the same factor, an effect of initiator amount on particle size reduction was obvious according to the results of sample 509C with a larger conversion ratio approaching 100%. Accordingly, the KPS content of 3wt% based on monomer weight used in sample 509C was chosen in other polymerizations.

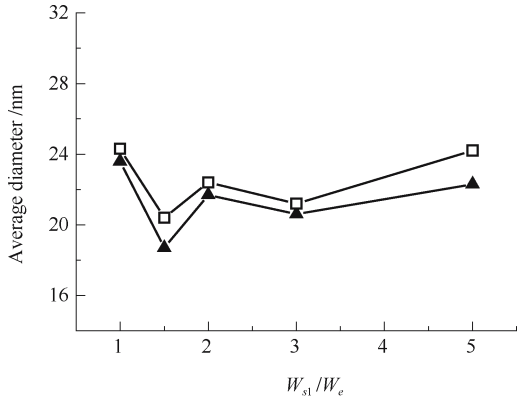

Fig. 1 Weight-average diameter (□) and number-average diameter (▲) of monodispersed PS particles at different W_{s1}/W_e

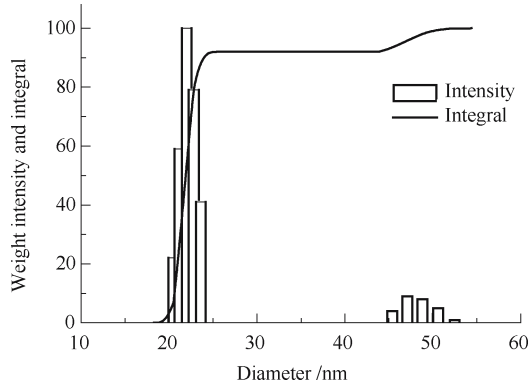

Fig. 2 Weight intensity and integral on size distribution of PS particles for sample 507 prepared by dropping all styrene of 5 g

Table 2 The average diameter and monodispersity index of PS nanoparticles prepared in polymerization systems[a] with different KPS weight

Sample No.	W_i (g)	D_n (nm)	D_w (nm)	D_w/D_n	C (%)
511B	0.05	5.3	10.6	1.98	79.6
510C	0.10	22.5	23.1	1.03	89.0
509C	0.15	23.6	24.3	1.03	99.5

a. Water, 100 mL; n-Butanol, 0.10 g; W_{s1}, 1.00 g; W_s, 5.00 g.

3.3 Influence of emulsifier amount

Stage 1 is a key period for the polymerization in preparing PS nanoparticles with a much smaller diameter and apparently, the emulsifier weight is also an important factor influencing the nucleation number and the resulting particle size. It has been demonstrated above that in the weight ratio of SDS and St_1, St_1 was not the only potential factor influencing particle size. Hence, the influences of the emulsifier amount were investigated while keeping the W_e/W_{s1} constant. Corresponding results are presented in Table 3 listing the amounts of SDS, St_1, St_2 and the proportions of SDS with total monomer weight. Moreover, the change of particle size is fully displayed in Fig. 3. The particle size distinctly presented a downward trend with the increase of SDS weight. When the SDS/St weight ratio (W_e/W_s) was increased to 0.30, the PS particles for sample 513B had a D_n of 18.7 nm similar to that of sample 510B mentioned above and a good monodispersity ($D_w/D_n = 1.07$), which was obtained in a polymerization

Table 3 The average diameter and monodispersity index of PS nanoparticles prepared in polymerization systems[a] with different SDS amount and same SDS/St_1 weight ratio

Sample No.	W_e (g)	W_{s1} (g)	W_{s2} (g)	W_e/W_s	D_n (nm)	D_w (nm)	D_w/D_n	C (%)
512E	0.15	0.15	4.85	0.03	47.0	47.0	1.00	96.3
512C	0.25	0.25	4.75	0.05	31.9	35.4	1.11	94.3
513A	0.50	0.50	4.50	0.10	23.5	24.7	1.05	96.0
512A	0.75	0.75	4.25	0.15	21.9	22.7	1.04	95.0
509C	1.00	1.00	4.00	0.20	23.6	24.3	1.03	99.5
513B	1.50	1.50	3.50	0.30	18.7	20.0	1.07	95.2

a. Water, 100 mL; KPS, 0.15 g; n-Butanol, 0.10 g; W_s, 5.00 g; W_e/W_{s1}, 1.0.

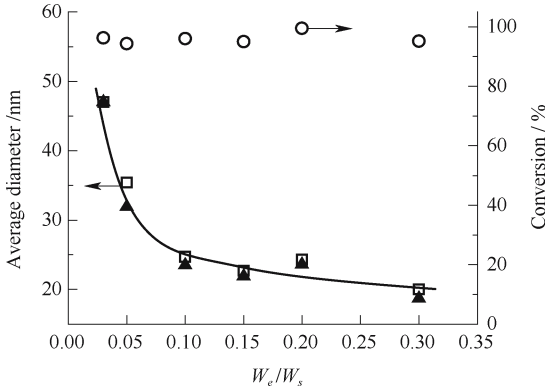

Fig. 3 Weight-average diameter (□) and number-average diameter (▲) of monodispersed PS particles with their monomer conversion ratio (○) at different SDS/St weight ratio

process with a final monomer conversion ratio higher than 95%. The morphology of sample 513B and its size and monodispersity can be directly observed in the TEM photograph shown in Fig. 4.

4 Conclusions

In the polymerization systems having smaller dosages of emulsifier SDS similar to conventional emulsion polymerization, the PS particles having a smaller diameter and good monodispersity can be prepared by adopting a particular monomer-added procedure. Particularly, the PS particles with D_n of 18.7 nm and D_w/D_n smaller than 1.1 were obtained under the conditions of SDS/St weight ratio of 0.2, St_1/St weight ratio of 1.5/5.0, and KPS amount of 3wt% based on the monomer. Moreover, it was concluded that dropping styrene in stage 1 at smaller amounts and not most or all the monomer can carry out the purpose of decreasing size and improving monodispersity of the PS particles, which makes the polymerization processes simpler.

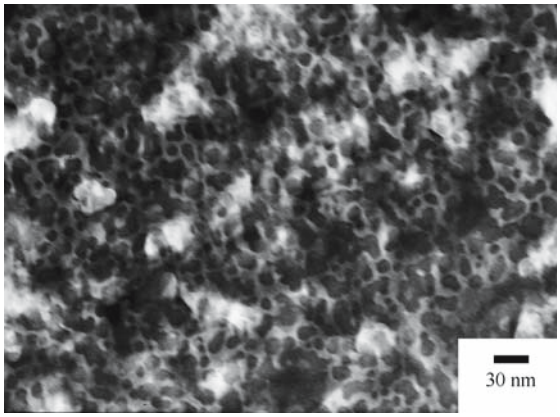

Fig. 4 TEM photograph of sample 513B prepared at W_e/W_s of 0.30, W_e of 5.00 g and W_e/W_{s1} of 1

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 90205015 and 50533020).

References

1. Kuo P L, Turro N J, Tseng C M, El-Aasser M S, Vanderhoff J W. Photoinitiated polymerization of styrene in microemulsions. Macromolecules, 1987, 20(6): 1216−1221
2. Lee S, Rudin A. The mechanism of core-shell inversion in two-stage latexes. Journal of Polymer Science Part A: Polymer Chemistry, 1992, 30 (5): 865−871
3. Gan L M, Lian N, Chew C H, Li G Z. Polymerization of styrene in a Winsor I-like system. Langmuir, 1994, 10(7): 2197−2201
4. Jang J, Ha H. Fabrication of hollow polystyrene nanospheres in microemulsion polymerization using triblock copolymers. Langmuir, 2002, 18(14): 5613−5618
5. Ming W, Zhao J, Lu X, Wang C, Fu S. Novel Characteristics of Polystyrene Microspheres Prepared by Microemulsion Polymerization. Macromolecules, 1996, 29(24): 7678−7682
6. Ming W, Jones F N, Fu S. High solids-content nanosize polymer latexes made by microemulsion polymerization. Macromolecular Chemistry and Physics, 1998, 199(6): 1075−1079
7. Zhang C H, Wang Q, Xia H S, Qiu G H. Ultrasonically induced microemulsion polymerization of styrene. European Polymer Journal, 2002, 38 (9): 1769−1776
8. Xu X J, Chew C H, Siow K S, Wong M K, Gan L M. Microemulsion Polymerization of Styrene for Obtaining High Ratios of Polystyrene/Surfactant. Langmuir, 1999, 15 (23): 8067–8071
9. He G, Pan Q. Synthesis of Polystyrene and Polystyrene/Poly (methyl methacrylate) Nanoparticles. Macromolecular Rapid Communications, 2004, 25(17): 1545−1548
10. Guo J S, Sudol E D, VANDERHOFF J W, El-Aasser M S. Particle nucleation and monomer partitioning in styrene O/W microemulsion polymerization. Journal of Polymer Science: Part A: Polymer Chemistry, 1992, 30(5): 691−702