Preparation of Micron-Size Monodispersed PS/P(St/MAA) Microspheres by Seeded Dispersion Polymerization

Hong-Tao Zhang, He Huang, Rong Sun, Jin-Xia Huang

Faculty of Chemistry and Materials Science, Hubei University, Wuhan 430062, People's Republic of China

ABSTRACT: Uniform polystyrene (PSt) particles with the size of 1.9 μm were first prepared via dispersion polymerization, and then used as the seeds in a second-stage dispersion copolymerization of styrene (St) and methacrylic acid (MAA) to produce carboxyl-carrying microspheres. The PSt seed particles were swollen by monomer mixture of St and MAA, including an oil-soluble initiator 2,2'-azobisiso-butyronitrile (AIBN), before polymerization. Finally, uniform PS/P(St/MAA) (polydispersity index, PDI = 1.02) microspheres with the size of 2.2 μm were obtained. The average particle size and size distribution of the final microspheres were investigated. MAA contents between 54 and 97 mg/g were detected from the PS/P(St/MAA) particles produced under different conditions. Dispersion medium has great influence on the kinetics of polymerization, due to its effect on the partitioning of monomers, solvents, and initiator in the particle phase, probably as well as on the conformation of the dispersion agent on the surface of the particles. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3586–3591, 2006

Key words: seeded dispersion polymerization; functional microsphere; styrene; methacrylic acid

INTRODUCTION

Several techniques have been developed to prepare micron-sized microspheres. Among them, dispersion polymerization is an effective way.[1] It is well-known that monodispersed microspheres have a variety of applications in the fields of calibration standards, analytical chemistry, bioengineering, coating, etc, due to their special properties, such as higher specific surface area, the ability of surface reaction, and stronger adsorption.[2]

One of the methods to make functional microspheres is copolymerization of two monomers, with one bearing a chemically reactive group, such as carboxyl,[3–6] amide,[7] sulfate, and hydroxyl.[8,9] However, there are fewer functional groups on the surface of a microsphere prepared by direct copolymerization than by seeded dispersion polymerization.[10–16] In addition, seeded dispersion polymerization has many other potential advantages in the preparation of micron-sized particles, compared with other methods, for example, the enhancement of exterior acid content on the surface of microsphere, uniformity of microsphere size, etc.

In seeded dispersion polymerization, the copolymerization of monomers with different water solubil-

ity has long been a challenge and remains an active research field. It was found that the incorporation of water-soluble monomer into the copolymer is very limited regardless of initial amount of water-soluble monomer loaded into the system.[17–19]

In our previous work, dispersion polymerization of styrene (St),[20] as well as the copolymerization of methyl methacrylate and acrylic acid in a polar medium,[21,22] was studied. In this work, we applied seeded dispersion polymerization to produce uniform PS/P(St/MAA) microspheres. First, micron-sized polystyrene (PSt) particles were prepared by dispersion polymerization. These uniform PSt particles were then used as the seeds for a second-stage dispersion copolymerization of St and MAA, which have different water solubility, in an ethanol/water medium. The effect of reaction parameters, including various weight ratios between PSt seed and monomer mixture of St and MAA, as well as the ratios between the two monomers, St and MAA, on the particle size and size distribution of the resulting microspheres were carefully investigated. The effect of dispersion medium on the kinetic of the polymerization is also reported.

EXPERIMENTAL

Materials

St monomer (industrial product) was washed with 10% sodium hydroxide aqueous solution, distilled under reduced pressure to remove the inhibitor, and then stored under refrigeration until use. 2,2'-Azobi-

siso-butyronitrile (AIBN, Shanghai Forth Chemical Plant, China) was purified by recrystallization in ethanol. Methacrylic acid (MAA) was purchased from Tianjing Bodi Chemical Ltd. Co. and treated by distillation under reduced pressure. Water was deionized before use. Poly(N-vinylpyrrolidone) (PVP) (M_n: 40,000, Wuhan Supply Station of Chemical Materials) and all other reagents were used as received.

Preparation of PSt seed

PSt seed particles were prepared by dispersion polymerization according to the recipe shown in Table I.

A 250-mL, four-neck, round-bottom flask equipped with an anchor-type agitator, a reflux condenser, and nitrogen inlet and outlet was employed to carry out the polymerization. PVP, dissolved in 100 mL of dispersion medium consisting of ethanol and water with a certain ratio, was first introduced into the reaction flask. Then the St monomer with dissolved AIBN was mixed with the dispersion medium. After purging with nitrogen more than 30 min at room temperature, the flask was immersed in a water bath at 70°C and stirred mechanically at a constant rate of 100 rpm for 12 h.

To test the influence of PVP molecules absorbed on the surface of PS seed particles on the second-stage polymerization, the seed particles were further treated by the following two methods.

In Method 1, the seed latex was deposited and washed with ethanol and then with H_2O. The weight ratio between the seed latex and ethanol or H_2O was 1:10. This process was repeated three times until no solid could be found in the dispersion medium. "Cleaned" PSt particles obtained in this way were expected and proved to have no "free" PVP molecules absorbed on the surface.[23]

In Method 2, the seed latex was deposited once and the supernatant was decanted. Then, the latex sediment was simply dispersed in the new dispersion medium of ethanol and H_2O by shaking to obtain the seed particles of PSt. Naturally, PSt particles thereby obtained will absorb more "free" PVP molecules on their surfaces.

Seeded dispersion copolymerization

All the seeded dispersion copolymerizations were carried out according to the standard recipe given in

TABLE I
Recipe for Preparing Polystyrene Seed Particles

Ingredient	Amount (g)
Ethanol	302
Water	38
St	150
PVP	10
AIBN	1.5

TABLE II
Recipe for Preparing PSt/(St + MAA) Microspheres at Various Weight Ratios Between PSt Seed and Monomer Mixture of St and MAA

Ingredient	Various weight ratios of PSt/(St + MAA)			
PSt (g)	1	1	1	0.26
St (g)	0.67	0.4	0.33	0.14
MAA (g)	0.33	0.2	0.17	7.48
AIBN (mg)	18.7	11.22	9.35	10/4
PSt/(St + MAA)	1/1	10/6	2/1	0.26

Polymerization time, 24 h; polymerization temperature, 70°C.

Table II. The system was kept for 24 h under stirring to ensure that the monomers were absorbed into the PSt seed particles, as much as possible, prior to the polymerization. The actual amount of latex that was needed for the seeded dispersion copolymerization is dependent on the solid content of the cleaned seed latex. Additional dispersion medium was added to the seed latices until the total amount of the dispersion medium was 12.5 g. The polymerizations were carried out in 2-oz bottles at 100 rpm for 24 h in a 70°C water bath. The conversions were measured by gravimetry.

Characterization

The particle size and distribution of microspheres were measured on SA-CP3, an instrument for particles size distribution measurement by centrifugation sedimentation. Particle size and size distribution of the copolymer were calculated with the following formulae:[24]

$$D_n = \sum_{n=1}^{n} di / n$$

$$D_w = \sum_{n=1}^{n} di^3 \bigg/ \sum_{n=1}^{n} di^4$$

$$\text{PDI} = D_w / D_n$$

where, D_n is number-average particle diameter, D_w is the weight-average particle diameter, PDI is the polydispersity index of the particles, and n is the total number of polymer particles measured.

Particle morphology was measured by transmission electron microscopy (TEM), JEM-100SX (JEOL, Tokyo, Japan). The particles size in the photograph was magnified 2000 times.
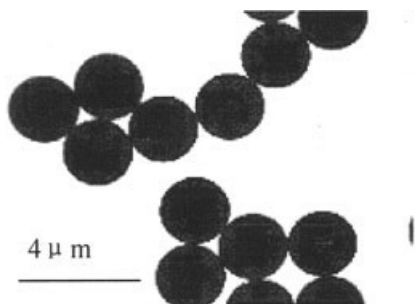
Figure 1 TEM images of PSt seed microspheres.

Conductometric titration

To determine the amount of carboxyl groups on the latex particles, 30 g of the latex (~5% solids) was titrated with 0.02N NaOH solution and then reversely titrated with hydrochloric acid. The conductance was monitored continuously. A detailed introduction of this method was provided elsewhere.[25]

Determination of conversion

Conversions were determined with a gravimetric method. The sample (about 1–2 g) was extracted after the onset of the reaction with certain time-intervals, and a drop of 1% hydroquinone solution promptly added to terminate the polymerization. Each sample was then dried under a vacuum at 70°C until the weight change was less than 0.001 g. The conversion was then calculated as follows[26]:

$$C = (M_2 - M_1 \times (W_2 + W_3)$$
$$- M_5 \times W_5)/(M_1 \times W_1 - M_6 \times W_6)$$

where, C is the monomer conversion, M_1 is the mass of the sample before drying, M_2 is the mass of the sample after drying, W_1 is the weight percentage of monomers in the reaction, W_2 is the weight percentage of PVP in the reactor, W_3 is the weight percentage of AIBN in the reactor, M_5 and M_6 are the mass of the seed particles after drying and before drying, and W_5 and W_6 are the weight percentage of seed particles before and after the reaction.

RESULTS AND DISCUSSION

Preparation of PSt seed microspheres

Figure 1 shows TEM images of PSt microspheres produced by dispersion polymerization under the conditions listed in Table I. The number-average diameter (D_n) and the PDI of the particles were 1.9 and 1.002 μm, respectively. Monodisperse PSt microspheres were obtained. These PSt microspheres, after being cleaned with Method 1 and 2 as mentioned earlier,

were used for seeded dispersion copolymerization of St and MAA in the next stage. It was noticed that the final outcome of the seeded dispersion copolymerization was very different. Serious coagulations occurred frequently when the seeded dispersion polymerization was carried out using the "cleaned" seed particles from Method 1, whereas stable dispersion systems were obtained by using seed particles of Method 2, suggesting that the absorption of more PVP molecules on the PSt seed particles is helpful to produce stable dispersions in the second-stage seeded dispersion copolymerization of St and MAA.

Preparation of PSt/(St + MAA) microspheres

Two factors, i.e., weight ratios of monomer mixture/seed latex and St/MAA, were considered while making the PSt/(St + MAA) microspheres. The former was first investigated and the ratio varied from 0.4 to 1 (see Table III).

Table III shows final conversion of monomers (St and MAA), latex stability, and diameters of the PSt/(St + MAA) microspheres produced under different ratios between PSt seed particle and monomer mixture. Figure 2 presents the TEM photographs of PSt/P(St-MAA) microspheres produced under these conditions.

It can be seen that the monodispersity of PSt/(St + MAA) microspheres decreased with the decreasing ratio between PSt seed and monomer mixture, and partial coagulation happened when the ratio reached 1/1. This should be straightforward. When more monomers were added to the PS seed latex, it required more dispersion stabilizer PVP to stabilize the whole system.

The influence of weight ratio of St to MAA on the particle size was also monitored. Table IV shows the recipe for preparing PSt/P(St-MAA) microspheres. The weight ratio of PSt seed/monomer mixture was set to be 2/1. The weight ratio of St/MAA was changed from 4/1 to 1/4 and the polymerizations were conducted at 70°C.

TABLE III
Monomer Conversion, Latex Stability, As Well As the D_n and PDI of the PSt/(St + MAA) Microspheres Obtained

PSt (St + MAA)	Conversion (%)	D_n (μm)	PDI	Colloidal stability
1/1	—	2.5	—	Partially coagulated
10/6	95.1	2.2	1.12	Stable
10/5	92.7	2.2	1.03	Stable
10/4	87.4	2.1	1.02	Stable

Polymerization time, 24 h; polymerization temperature, 70°C.
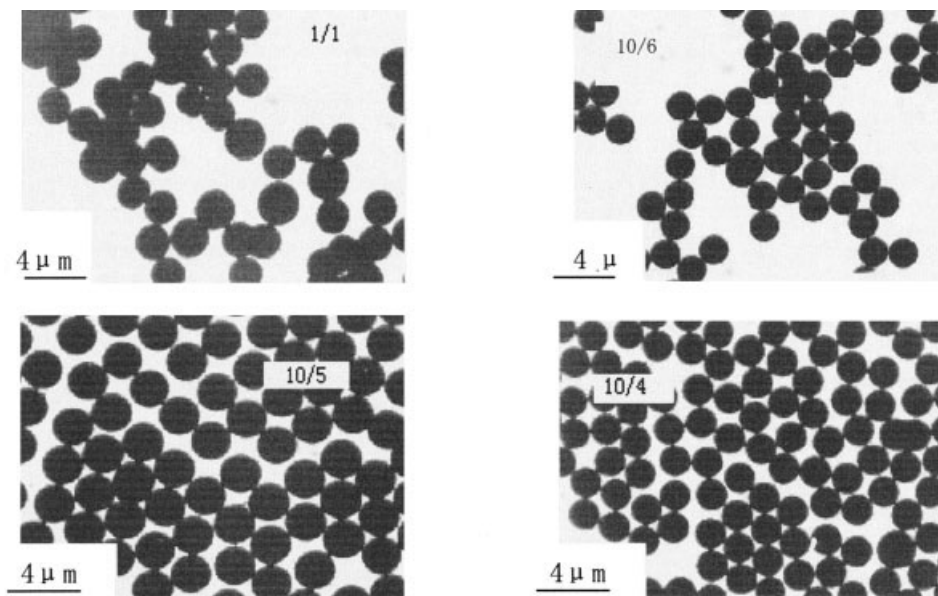
Figure 2 TEM images of PSt/P(St-MAA) composite particles produced under the conditions listed in Table III.

Figure 3 shows TEM images of PSt/P(St + MAA) microspheres produced under the conditions listed in Table IV. Monodisperse microspheres were produced, with partial coagulation occurring when St/MAA = 1/4. This suggests that induction of more hydrophilic MAA monomers facilitates the adhesion among particles.

In summary, to produce stable and monodisperse PSt/P(St + MAA) microspheres, the optimum weight ratios of PSt seed/monomer mixture and St/MAA are around 2/1, and monodispersed PSt/P(St-MAA) microspheres with 2.2 μm in D_n and 1.02 in PDI were obtained. Titratable MAA contents, i.e., surface bound and physically absorbed,[18] between 54 and 97 mg/g were detected for the particles produced under these conditions.

Effect of dispersion medium on the kinetics of copolymerization

It is generally accepted that dispersion polymerization starts as a homogeneous process, i.e., it takes place in

TABLE IV
Recipe for Preparation of PSt/P(St + MAA)
Microspheres at Various Weight Ratios of St/MAA

Ingredient	Various weight ratios of St/MAA		
PSt (g)	1	1	1
St (g)	0.1	0.33	0.4
MAA (g)	0.4	0.17	0.1
AIBN (mg)	18.7	9.35	7.48
St/MAA	1/4	2/1	4/1

Polymerization time, 24 h; polymerization temperature, 70°C.

the solution (continuous) phase, at the very beginning, but it becomes a heterogeneous process at the early stages of the reaction. More specifically, phase separation occurs as soon as the generated polymer oligomers, growing beyond a critical chain length, precipitate from the continuous phase, which are stabilized by the dispersion agent. Because of this characteristic, solvent (dispersion medium) solvency plays a key role in controlling the rate of polymerization, particle size distribution, and the kinetic of particle formation.[16,26–28]

In this study, we used a mixture of ethanol and water as dispersion medium. By changing the volumetric ratio of ethanol/water, the solvency of the medium can be adjusted. Figure 4 presents kinetic curves of seeded dispersion copolymerization of St and MAA in two media with different ethanol/water volumetric ratios. It can be seen that the polymerization rate in the medium with 60/40 ethanol/water was much faster than that in the 70/30 one. Most strikingly, the final monomer conversion reached 95.2% in the former case, while only 28% in the latter one. Obviously, these two curves exhibited very different features, suggesting that quite different polymerization took place when the ethanol/water volumetric ratios were different.

The solubility parameters of ethanol and water are 25.97 and 47.43 MPa$^{1/2}$, respectively.[29] The empirical solubility parameter δ of the mixture, which is useful to estimate the initial solvency of the medium, can be calculated by:[30]

$$\delta = (\nu_e \delta_e^2 + \nu_w \delta_w^2)^{1/2}$$
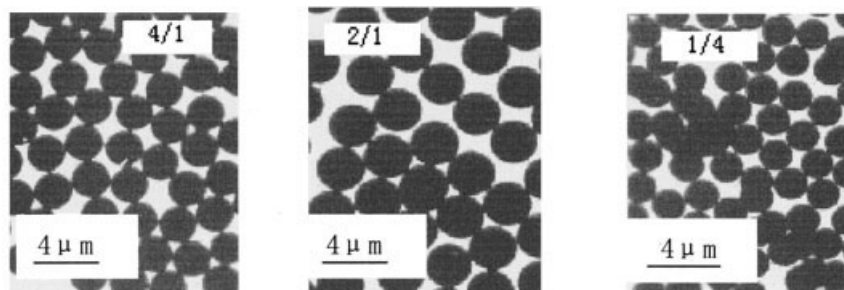
Figure 3 TEM images of PSt/P(St + MAA) microspheres produced under the conditions listed in Table IV.

where v_e and v_w are the volume fractions, δ_e and δ_w are the solubility parameters of ethanol and water, respectively. Then the calculated solubility parameters ($MPa^{1/2}$) of dispersion media with ethanol/water ratio of 60/40 and 70/30 were 36.09 and 34.10 $MPa^{1/2}$, respectively.

Compared to the case where the ethanol/water ratio is 70/30, the polymerization rate in the medium with 60/40 ethanol/water is much faster, suggesting that polymerization rate increased with increasing solubility parameter or medium solvency. This finding is consistent with the experimental result of Ho et al.,[26] who carried out the dispersion polymerization of St in three different alcohols. But, obviously, our system is much more complicated due to the addition of a second water-soluble monomer and a second solvent water. There might be a number of reasons behind this phenomenon, but here, we discuss the role of one component of the dispersion medium, water.

Water is a poor solvent for St monomer or PSt polymer, but it is a good solvent for MAA monomer and PMAA polymer. When more water is present in the medium, for example, the medium with 60/40 ethanol/water, St monomer would prefer to stay in the seed PSt particles, i.e., there would be more St monomers in the PSt seed particles. It is thus expected that the polymerization rate would be higher when the monomer concentration in the particle phase is higher.

In addition, water is also a poor solvent for the oil soluble initiator AIBN, suggesting that AIBN would also prefer to stay in the PSt seed particles as St monomer does while mixing. This will obviously increase the initiator concentration in the particle phase, and thus increase the polymerization rate.

Furthermore, less ethanol would mix with PSt seed particles when more water exists in the medium. This will increase the viscosity of the particle phase, and thereby decrease the termination of free radicals. Therefore, the polymerization rate will increase due to the so-called "gel effect". Of course, as discussed above, more water in the medium would lead to a greater concentration of St monomer in the particles, reducing the internal viscosity. This would decrease the gel effect initially. Unfortunately, it is not practical to get quantitative data to compare these two factors and determine which one is predominant. Nevertheless, the two reasons mentioned above, i.e., greater concentrations of St monomer and initiator in the particles, are enough to interpret why the polymerization rate in the medium with 60/40 ethanol/water was much faster than that in the 70/30 one.

Finally, because of the good solubility of PVP in water, a larger amount of water might also "open up" the dispersion agent layer on the surface of the PSt seed particles, which promotes the entry of St monomers and initiator AIBN into PSt particles. This effect, maybe minor of course, also leads to the increase of polymerization rate when the medium of ethanol/water (60/40) is used.

CONCLUSIONS

Micron-size monodispersed PSt/(St + MAA) microspheres were successfully prepared via seeded dispersion copolymerization in aqueous alcohol media with AIBN as initiator. The influence of weight ratio between PSt seed particle and monomer mixture and St/MAA ratio on particle size, size distribution, and the stability of latex produced were investigated, and
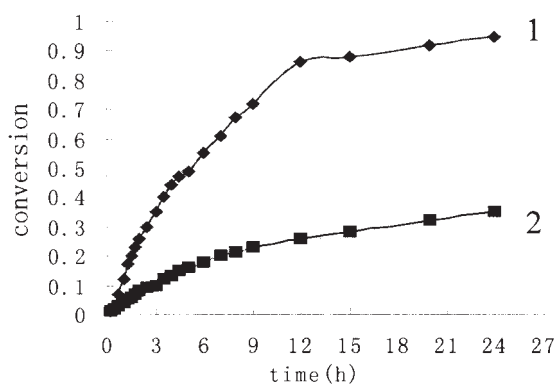
Figure 4 Kinetic curves with different ethanol/water ratio. (1) 60/40 and (2) 70/30.

an optimum ratio of 2/1 for both has been suggested, to make stable and monodisperse particles. Caboxyl contents between 54 and 97 mg/g were detected from the particles produced under different conditions. The polymerization rate in the medium with 60/40 ethanol/water was much faster than that in the medium with 70/30 ethanol/water, and the final monomer conversion was much higher, up to 95.2%, in the former case, while only 28% was obtained in the latter one, suggesting that dispersion medium has great influence on the kinetic of polymerization, This might be largely attributed to the variation of partitioning of monomers, initiator and solvent, as well as the conformation of the dispersion agent on the surface of the particles due to the addition of water.

References

1. Barrett, K. E. J. Dispersion Polymerization in Organic Media; Wiley: New York, 1975.
2. Candau, F.; Ottewill R. H. NATO AST Series C303; Kluwer: Dordrecht, 1990.
3. Muroi, S. J Appl Polym Sci 1966, 10, 713.
4. Egusa, S.; Makuuchi, K. J Polym Sci Polym Chem Ed 1982, 20, 836.
5. Hoy, K. L. J Coat Technol 1979, 51, 27.
6. Ohtsuka, Y.; Kawaguchi, H.; Sugi, Y. J Appl Polym Sci 1981, 26, 1637.
7. Tsaur, S. L.; Fitch, R. M. J Colloid Interface Sci 1987, 115, 450.
8. Kawaguchi, H.; Sugi, Y.; Ohtsuka, Y. J Appl Polym Sci 1981, 26, 1649.
9. Okubo, M.; Ymada, A.; Matsumoto, T. J Polym Sci Polym Chem Ed 1980, 16, 3219.
10. Wang, D.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Appl Polym Sci 2002, 84, 2721.
11. Wang, D.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Appl Polym Sci 2002, 84, 2710.
12. Lu, Y. Y. Ph.D. Dissertation, Lehigh University, 1988.
13. Okubo, M.; Ikegami, K.; Yamamoto, Y. Colloid Polym Sci 1989, 267, 193.
14. Okubo, M.; Ikegami, K.; Yamamoto, Y. Colloid Polym Sci 1991, 269, 217.
15. Wang, D.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Appl Polym Sci 2002, 84, 2692.
16. Tuncel, A.; Kahraman, R.; Erhan, P. J Appl Polym Sci 1994, 51, 1485.
17. Zhang, H. T.; Yuan, X. Y.; Huang J. X. React Funct Polym 2004, 59, 23.
18. Zhang, H. T.; Huang, H.; LV, R.; Chen, M. Colloids Surf A 2005, 253, 217.
19. Zhang, H. T.; LV, R.; Chen, M. Chem J Chin Univ 2004, 25, 366.
20. Zhang, H. T.; Huang, J. X.; Jiang, B. B.; Li, X. Q. Chin J Appl Chem 2001, 18, 726.
21. Huang, J. X.; Yuan, X. Y.; Yu, X. L.; Zhang, H. T. Polym Int 2003, 52, 819.
22. Zhang, H. T.; Huang, J. X.; Jiang, B. B. J Appl Polym Sci 2002, 85, 2230.
23. Sun, R. Master Thesis, Hu Bei University, 2004.
24. Kiatkamjornwong, S.; Kongsupapsiri, C. Polym Int 2000, 49, 1395.
25. Hen, J. J Colloid Interface Sci 1974, 49, 425.
26. Ho, C. H.; Chen, S. A.; Amiridis, M. D.; Vanzee, J. W. J Polym Sci Part A: Polym Chem 1997, 35, 2907.
27. Shen, S.; Sudol, E. D.; El-Aasser M. S. J. J Polym Sci Polym Chem Ed 1994, 32, 1087.
28. Shen, S.; Sudol, E. D.; EL-Aasser M. S. J Polym Sci Polym Chem Ed 1993, 31, 1393.
29. He, J. M.; Chen, W. X.; Dong, X. X. Polymer Chemistry; Fudan University Press: Shanghai, 1990.
30. Paine, A. J. Macromolecules 1990, 23, 3109.