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Uniform Polystyrene Particles by Dispersion Polymerization in Different Dispersion Medium

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Summary

Using PVP K-30 as steric stabilizer and AIBN as initiator, uniform polystyrene (PS) particles were prepared by dispersion polymerization of styrene in ethanol/water and isopropanol/water media. The effects of initiator and stabilizer concentration, alcohol/ water volume ratio on the average sizes and size range of PS particles were investigated. Unifrom PS particles in the size range of 0.7−1.7 μm were obtained. The results showed that higher stabilizer concentration led to PS particles with smaller average sizes, and higher initiator concentration caused greater average particle sizes. It was also found that the average sizes reduced and size ranges became narrow as the polarity (solubility parameter) of dispersion medium employed was increased.

Introduction

Uniform polymer particles have found a wide variety of applications in the biomedical treatment, chromatography, information industries and electronic fields [1−3]. In the last decade, uniform polymer particles were widely used as templates for preparation of three-dimensionally ordered macroporous materials [4−5]. As a consequence, preparation techniques and property control of uniform polymer particles have become more important.

Uniform polymer particles in the micron size range could be prepared by multistage seed emulsion polymerization and dispersion polymerization. But the former technique is time-consuming and is often difficult to be carried out. In contrast, dispersion polymerization is an attractive route for producing uniform polymer particles with diameter of 0.5−10 μm because of its single-step process. In dispersion polymerization process, the reaction mixture is a homogeneous solution containing monomer dissolved in a dispersion medium, and the final polymers precipitate as solid spherical particles in the presence of a suitable steric stabilizer [6−7].

Styrene monomer has been polymerized in alcohols in the presence of steric stabilizers such as (hydroxy-propyl)cellulose (HPC), poly(acry1ic acid) (PAA), or poly(N-vinylpyrrolidone) (PVP) [8−11]. In favorable circumstances, these PS particles are of very narrow size distribution, or even monodisperse. For example, Ober et al [12] prepared monosize polystyrene particles up to 9 μm in ether/alcohol systems in the presence of different nonionic cellulosic polymers as steric stabilizers. Using poly(N-vinylpyrrolidone) as a steric stabilizer, Paine and co-workers [6] produced monosize polystyrene particles with diameter up to 18 μm in alcoholic medium. Also, Paine has successfully proposed a simple mathematical model to predict the particle size for dispersion polymerization of styrene in polar solvents [7]. More recently, Xu et al [13] reported monosize polystyrene particles with diameters of 200–500 nm were prepared by dispersion polymerization with microwave irradiation. Choe et al [14] using a vinyl-terminated polyurethane macromonomer as a stabilizer, synthesized uniform PS particles having the weight-average diameter of 1.2 μm by dispersion polymerization.

The objective of this work is to find a more simple and effective method to fabrication of uniform PS particles. Styrene monomer was polymerized in ethanol/water and isopropanol/ water media by dispersion polymerization. The effects of alcohol/water volume ratio, stabilizer and initiator concentration on the number average diameters and uniformity of polystyrene particles were evaluated.

Experimental

Materials

All materials are purchased form Sinopharm Chemical Reagent Co. Ltd, China. Styrene was treated with aqueous NaOH to remove the inhibitor, then was distilled under vacuum and stored in the refrigerator until it was used. 2,2′-azo-bis-isobutyronitrile (AIBN) was re-crystallized from methanol and used as the initiator. All other materials were used without further purification, including poly (vinylpyrrolidone) (PVP K-30), ethanol and isopropanol.

Dispersion Polymerization

Dispersion polymerization was carried out in a 100 cm^3 three neck reactor, which are equipped with an anchor-shaped stirrer and condenser. In a typical procedure, certain amount of PVP K-30 was dissolved in 50 cm^3 alcohol/water mixture to obtain the water phase; and the oil phase was prepared by dissolving AIBN in 5 cm^3 styrene monomer. The two phases were mixed and charged into the reactor. The mixtures were stirred at a speed of 150 rpm and purged with nitrogen for 15 min, then polymerization were conducted at a constant temperature of 75°C for 12 h. After polymerization, the polystyrene particles were washed two times with deionized water, and two times with methanol, and then were dried in vacuum oven at 50°C. The stabilizer and initiator concentration, the alcohol/water volume ratio were changed to evaluate their effects on the average sizes and size distribution of PS particles. The monomer concentration was kept at a constant value of 0.87 mol/L.

Transmission electron microscopy

Average sizes and size range of polystyrene particles were evaluated by transmission electron microscopy (TEM). The polystyrene particles were dispersed in ethanol by sonication, and the dispersed solution was spread onto 200-mesh gilder copper TEM grids and air dried before TEM measurement. TEM micrographs were obtained on a JEOL model 1200EX instrument operated at an accelerating voltage at 160 kV. The number average diameters (D_n) were computed over more than 100 PS particles. The standard deviation (δ) and the coefficient of variation (ε) were calculated as follows:

$$\delta = \left[\frac{\sum_{i=1}^{n} (D_i - D_n)^2}{n-1} \right]^{1/2} \qquad \varepsilon = \delta / D_n \tag{1}$$

Where D_i is the diameter of PS particles, and n is the number of particles.

Results and Discussion

Effect of Stabilizer Concentration

In this section, effect of stabilizer concentration on average sizes and size range of PS particles was evaluated at a constant alcohol/water volume ratio and initiator concentration (1.0 mol %). Dispersion polymerizations of styrene were performed with four different stabilizer concentrations (5.0×10^{-3}, 10.0×10^{-3}, 15.0×10^{-3}, 20.0×10^{-3} g/cm^3) in ethanol and isopropanol/water media. It should be noted that stabilizer PVP K-30 could be dissolved in dispersion media of ethanol and isopropanol/water without any difficulties. The TEM photographs, average diameter and size range of PS particles with different stabilizer concentrations were shown in Figure 1 and Table 1, respectively.

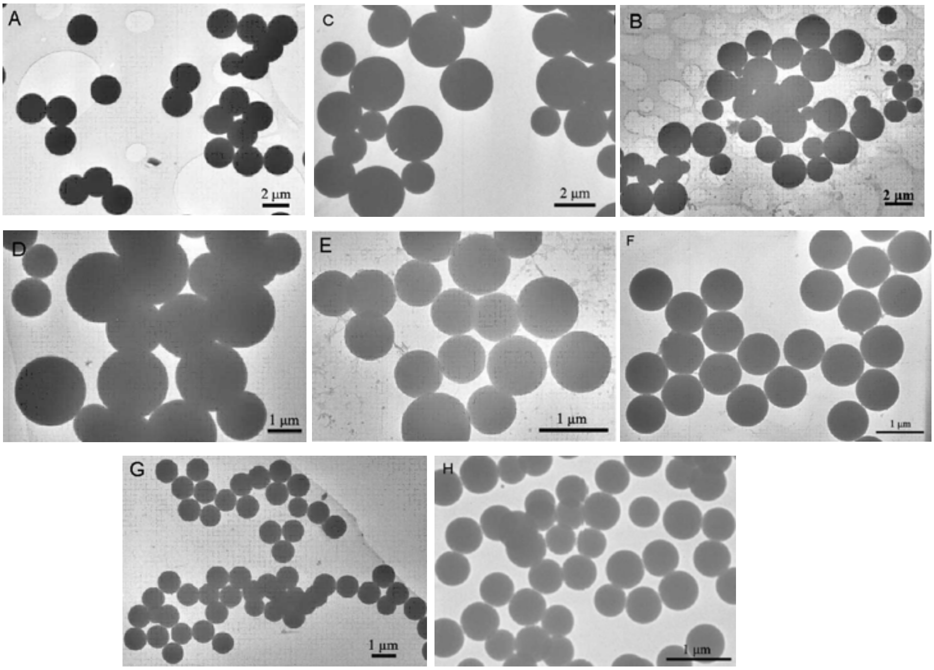

Figure 1 TEM photographs of PS particles prepared with different stabilizer concentration (A–D: 50/0 ethanol medium; E–H: 35/15 isopropanol/water medium). (A) and (E) 5.0×10^{-3} g/cm^3; (B) and (F) 10.0×10^{-3} g/cm^3; (C) and (G) 15.0×10^{-3} g/cm^3; (D) and (H) 20.0×10^{-3} g/cm^3.

As can be seen in Table 1, the number average diameters of PS particles reduced with increasing stabilizer concentration for the two dispersion media. Moreover, an approximate linear correlation was observed between the stabilizer concentrations and the average sizes from Figure 2. The results are in accord with that drawn by Tuncel et al [10]. It may be explained by the fact that dispersion polymerization begins and progresses around the stabilizer chains. During the nucleation period, the stabilizer chains form a structure that acts as a skeleton for PS particle growth. The number of nuclei increases on raising stabilizer concentration, which leads to more particles but with smaller size. In addition, higher PVP concentration causes higher viscosity of the dispersion medium and consequently, greater resistance for particle collision.

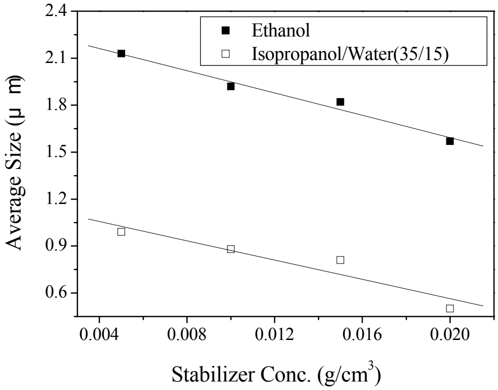

Figure 2 Effect of stabilizer concentration on average particle sizes.

Table 1 Effects of Stabilizer Concentration on Average Diameters and Size Range

Stabilizer Conc (g/cm^3)	Yield of PS Particles (%)	D_n (μm)	δ (μm)	ε (%)	Size Range (μm)
		Dispersion Medium: Ethanol			
5.0×10^{-3}	82.2	2.13	0.176	8.26	1.55 – 2.16
10.0×10^{-3}	76.8	1.92	0.482	25.1	0.95 – 2.52
15.0×10^{-3}	78.0	1.82	0.487	26.8	1.07 – 2.67
20.0×10^{-3}	89.6	1.57	0.315	20.1	0.98 – 2.10
		Dispersion Medium: Isopropanol / Water (35/15, v/v)			
5.0×10^{-3}	75.5	0.99	0.532	53.7	0.50 – 2.25
10.0×10^{-3}	67.3	0.88	—	—	Monosize
15.0×10^{-3}	85.2	0.81	—	—	Monosize
20.0×10^{-3}	90.6	0.50	0.096	19.2	0.39 – 0.62

Reactive temperature and time: 75°C, 12 h; monomer and initiator concentration: 0.87 mol/L, 1.0 mol %.

Although a decline was observed in the average particle sizes for ethanol medium, the coefficient of variation increased with increasing stabilizer concentration in this dispersion medium. However, uniform PS particles could be prepared in isopropanol/water system with suitable stabilizer concentration (10.0×10^{-3}, 15.0×10^{-3} g/cm^3). This fact approved the opinion that the most proper dispersion medium for preparation of uniform polystyrene particles was isopropanol/water system [11]. In addition, it should be noticed that relatively small particles were obtained in the isopropanol/ water medium. Different solubility parameters of ethanol (12.7) and isopropanol/water (35/15, 16.0) may responsible for the discrepancy of particle sizes, which will be discussed in detail in the following section.

Effect of Alcohol / Water Ratio

It is well known that solubility of monomer strongly depends on the polarity of the dispersion medium, which has a direct effect on the average sizes and size distribution of the final polymer particles [15]. Polarity of dispersion medium can be characterized by its solubility parameter. The greater the solubility parameter, the stronger the polarity of the dispersion medium is. Thus, in this section, the feed volume ratios of alcohol and water were changed to investigate the effect of polarity of dispersion medium on the average diameter and size distribution of PS particles. The solubility parameters of various media were calculated based on the information in Reference [16], and were given in Table 2. TEM photographs of PS particles prepared in different dispersion media were presented in Figure 3.

Table 2 Effects of Alcohol / Water Ratio on Average Diameters and Size Range

Alcohol/Water Ratio (v/v)	Solubility Parameter $(cal/cm^3)^{1/2}$	Yield of PS Particles (%)	D_n (μm)	δ (μm)	ε (%)	Size Range (μm)
		Dispersion Medium: Ethanol / Water				
50 / 0	12.7	78.0	1.82	0.487	26.8	1.07 – 2.67
45 / 5	14.1	82.4	0.74	0.086	11.6	0.52 – 0.82
40/10	15.4	73.9	0.43	0.047	10.9	0.32 – 0.48
35/15	18.5	67.2	0.41	0.044	10.7	0.30 – 0.46
		Dispersion Medium: Isopropanol / Water				
50 / 0	11.5	90.2	1.65	0.411	24.9	0.65 – 1.95
45 / 5	13.2	76.9	1.02	0.089	8.2	0.86 – 1.20
40/10	14.7	72.7	0.72	—	—	Monosize
35/15	16.0	85.2	0.81	—	—	Monosize

Monomer, initiator and stabilizer concentration are 0.87 mol/L; 1.0 mol %; 15.0×10^{-3} g/cm^3, respectively.

Varying alcohol/water volume ratio significantly changed the average diameter and size range of polystyrene particles. Although there are some scatters in the data of isopropanol/water medium, the average particle sizes reduce and size ranges become narrow as the solubility parameter of the dispersion medium employed is increased, namely, as the water content is increased. This behavior has been explained by Tuncel et al [10]. The formed PS chains are relatively apolar since styrene is more apolar than ethanol or isopropanol. These chains can reach relatively higher molecular weights by remaining in the dissolved form in isopropanol/water or ethanol/water media having more apolar character (less amount of water). Then, nucleation occurs at relatively higher molecular weights due to higher solubility of polystyrene chains in relatively apolar dispersion medium. As a result, formation of fewer nuclei leads to fewer PS particles but larger in their diameters. The nucleation process occurs at lower molecular weights of PS chains due to the declining solubility of those in the dispersion media with increasing water content. This effect leads to the generation of more particle nuclei and consequently to smaller particles with increasing water concentration.

Wide size ranges were observed when pure ethanol or isopropanol was used as the dispersion media. But uniformity was achieved especially with 40/10 and 35/15 isopropanol/water ratios. With water content in isopropanol/water mixture increasing, the size distribution become narrow (45/5, v/v), and then PS particles tend to be uniform (40/10, 35/15, v/v). In ethanol/water medium, although uniform particles can not be obtained, it should be noted that particles with diameter smaller than 0.5 μm and narrow size range can be produced (40/10, 35/15, v/v). It is well known that preparation of monodisperse particles smaller than 0.5 μm via dispersion polymerization is particularly challenging. Therefore, it seems likely that further work aimed at preparation of monodisperse PS particles smaller than 0.5 μm in 40/10 and 35/15 ethanol/water medium would be very valuable.

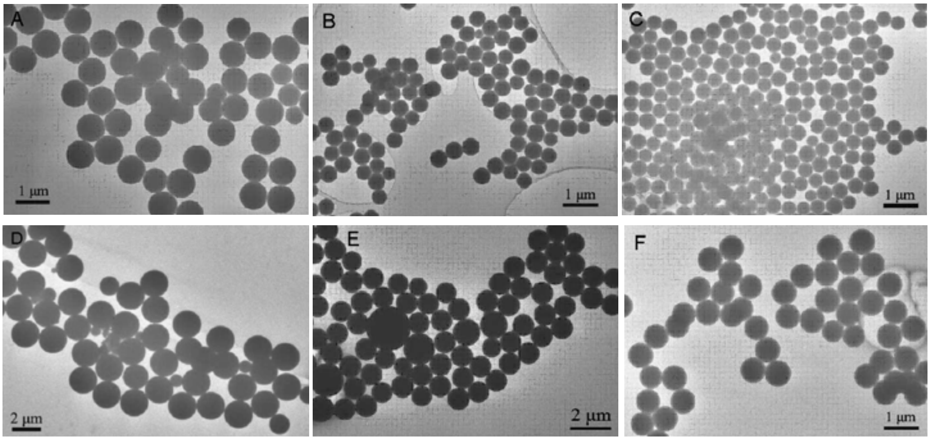

Figure 3 TEM photographs of particles prepared with different alcohol/water volume ratio. (A) 45/5 ethanol/water; (B) 40/10 ethanol/water; (C) 35/15 ethanol/water; (D)50/0 isopropanol/ water; (E) 45/5 isopropanol/water; (F) 40/10 isopropanol/water.

Initiator Concentration

In dispersion polymerization, nucleation or phase separation occurs when polymer chains reach a critical molecular weight and they become insoluble in the dispersion medium. Initiator (AIBN) concentration significantly influences molecular weight of polystyrene and consequently, its solubility in dispersion medium. Therefore, in this section, PS particles were prepared with different initiator concentration (i.e., 0.5, 1.0, 1.5, 2.0 mol %) at a constant stabilizer concentration and alcohol/ water volume ratio. The TEM photographs, the average sizes and size range were presented in Table 3 and Figure 4, respectively.

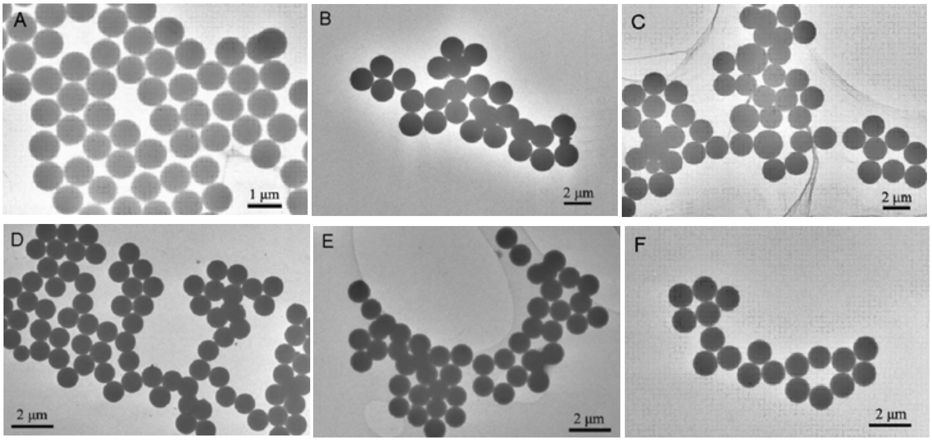

Figure 4 TEM photographs of particles prepared with different initiator concentration (A–C: in 50/0 ethanol/water medium; D–F: in 45/5 isopropanol/water medium). (A)1.0 mol %; (B) and (E) 1.5 mol %; (C) and (F) 2.0 mol %; (D) 0.5 mol %.

As seen here, apart from 0.5 mol % in ethanol/water system, the average particle sizes rise with increasing initiator concentration. This is an expected behavior and in agreement with result of Ober et al [17]. Higher initiator concentration caused greater free radical concentration, namely, polymerization started with more radicals per unit volume when high initiator concentration was employed. This results in polymer chains with lower molecular weight, which are more soluble in the two dispersion media. Therefore, at higher initiator concentration, fewer nuclei are formed due to low concentration of high molecular weight chains in the dispersion medium, which leads to fewer particles but larger in its diameter.

In this section, two different dispersion media were utilized to examine the effect of initiator on the average sizes and size range. The dispersion medium containing 90 % isopropanol and 10 % water may be considered as a more polar medium compared to ethanol (see Table 2). This results that the average particle sizes from the former

Table 3 Effects of Initiator Concentration on Average Diameters and Size Range

Initiator Conc. (mol %)	Yield of PS Particles (%)	D_n (μm)	δ (μm)	ε (%)	Size Range (μm)
		Dispersion Medium: Ethanol			
0.5	81.3	0.84	—	—	Monosize
1.0	78.0	1.82	0.487	26.8	1.07 – 2.67
1.5	69.5	1.65	—	—	Monosize
2.0	78.8	1.72	0.458	26.6	0.95 – 2.40
		Dispersion Medium: Isopropanol / Water (45/5, v/v)			
0.5	75.5	0.96	—	—	Monosize
1.0	76.9	1.02	0.089	8.7	0.86 – 1.2
1.5	85.2	1.07	—	—	Monosize
2.0	90.6	1.20	—	—	Monosize

Monomer, and stabilizer concentration are 0.87 mol/L; 15.0×10^{-3} g/cm^3, respectively.

medium are slightly larger than that from the latter. Furthermore, uniform particles with diameter in the size range of 0.84−1.65 μm can be produced at a suitable initiator concentration in the two dispersion media. Undoubtedly, initiator concentration has a direct effect on average sizes and uniformity of PS particles. This will be helpful to prepare uniform PS particles by the simple and effective technique.

Conclusion

In this study, uniform polystyrene particles were prepared by dispersion polymerization in ethanol/water and isopropanol/water media. Effects of initiator and stabilizer concentration, and alcohol/water volume ratio on the average sizes and size range of PS particles were investigated. Some results can be concluded as follows:

1. Higher stabilizer concentration leads to smaller average particle sizes. Moreover, stabilizer concentration can be optimized to achieve uniformity by using isopropanol/water as dispersion medium.
2. The average sizes reduce and size ranges become narrow as the solubility parameter of the media employed is increased (or water content is increased) in the two dispersion media.
3. Initiator concentration is one of the key parameters that significantly influences the average sizes and uniformity of PS particles. Higher initiator concentration causes greater average particle size.

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