Controllable Preparation of Monodisperse Polystyrene Microspheres with Different Sizes by Dispersion Polymerization

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Summary: Monodisperse polystyrene (PS) microspheres with different sizes were prepared by dispersion polymerization in dispersion media of ethanol/water and isopropayl alcohol/water, respectively. The effect of polarity of the dispersion medium, stabilizer and initiator concentration on the average sizes and size range were evaluated. The results show that monodisperse PS microspheres with different sizes could be prepared in dispersion media of ethanol and isopropyl alcohol/water when appropriate initiator and stabilizer concentrations were employed, and the latter is a more appropriate medium to prepare uniform PS microspheres. It was found that the microsphere sizes reduced with increasing water content in the dispersion medium. Furthermore, in isopropyl alcohol/water dispersions, the average sizes decreased with increasing stabilizer concentration.

Keywords: dispersions; monodispersity; polarity; polystyrene; size range

Introduction

Monodisperse polymer microspheres have received great attention due to their extensive applications in biomedical field, information industry, chromatographic separation, electric and electronic fields.[1–3] In monodisperse polymer microspheres, uniform polystyrene (PS) microspheres are also used as sacrificial materials and exhibit the most extensively application promise. For example, monodisperse PS microspheres have been widely used as colloidal crystal templates for preparing three dimensionally ordered macroporous materials.[4–6] Furthermore, uniform PS microspheres were also employed as templates for successive seed swelling techniques to yield larger uniform microspheres or porous materials.[7–9] In accord with their expanded applications, preparation techniques of PS microspheres with narrow size distributions have been the subject of both applied and fundamental research for many years.

Up to now, preparation techniques of uniform PS microspheres include microemulsion polymerization,[10] emulsifier-free emulsion polymerization,[11] seed emulsion polymerization,[12] and dispersion polymerization.[13–14] The first two methods are convenient for producing PS microspheres of submicrometer size, but low stability and solid content are two problems to be further solved. Seed emulsion polymerization developed by Ugelstad and his coworkers was the first successful technique for producing monosize polymeric microspheres in the range of 0.2–1.5 μm.[15] Using a successive swelling process, micrometer-size PS microspheres as large as 50 μm can be produced, however, this procedure is time-consuming and difficult to perform.[16] Dispersion polymerization is an attractive

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technique for producing uniform PS microspheres with diameters of 0.5–10 μm due to its single-step process. This procedure involves the polymerization of monomer dissolved in a solvent or solvent mixture in the presence of a stabilizer. Using polyacrylic acid as a stabilizer, Piskin et al. prepared monosize PS microspheres in an alcohol/water dispersion medium.[17] Recently, some new developments for preparing monodisperse PS microspheres have been achieved. For example, Choe et al.[18] prepared monodisperse PS microspheres by dispersion polymerization, using a vinyl-terminated polyurethane macromonomer as a stabilizer. Also, other macromonomers such as poly(oxyethylene),[19] poly(*N*-isopropylacrylamide),[20] and poly (2-oxazoline)[21] and their derivatives have been used as stabilizers in dispersion polymerization to prepare monodisperse polymer microspheres in polar solvents. Moreover, Xu's research group[22] produced monodisperse PS microspheres by dispersion polymerization with microwave irradiation. Here, the purpose of this work is to find a simple way and explore optimal conditions for producing monodisperse PS microspheres.

Experimental Part

Materials

Styrene (St, ≥99%, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) was extracted with 5% (w/w) sodium hydroxide solution to remove the inhibitor, and then washed with deionized water until neutral. After drying with anhydrous magnesium sulfate, styrene was distilled under vacuum and stored in the refrigerator. 2,2′-Azo-bis-isobutyronitrile (AIBN) was purchased from Linfeng Chem Co. Ltd, China. It was re-crystallized from methanol and used as the initiator. All other materials were used without further purification, including poly(vinylpyrrolidone) (PVP K-30, Sinopharm Chemical Reagent, China), ethanol (≥99.7%, Sinopharm Chemical Reagent, Hangzhou, China), and isopropyl alcohol (≥99.7%, Shuanlin Chemical Reagent, China).

Preparation of PS Microspheres

A certain volume of the dispersion medium (40 mL for ethanol/water, and 50 mL for isopropyl alcohol/water) and PVP K-30 were poured into a 100 mL glass reactor equipped with an anchor-shaped stirrer and a condenser. Styrene (5 mL) was then added, together with an appropriate weight of AIBN. After stirring at 150 rpm and purging with argon for 15 min, the mixtures were heated to 70 °C for 12 h. The products were washed twice with deionized water and twice with methanol. Finally, PS microspheres were dried in a vacuum oven at 50 °C. Reactions were carried out in two different dispersion media: ethanol/water and isopropyl alcohol/water mixture, respectively. The concentration of initiator and stabilizer, and the alcohol/water ratio, were changed to evaluate the effect of these parameters on the size and size distribution of the PS microspheres. The experimental conditions are presented in Table 1.

Characterization

The size and size distribution of the PS microspheres were determined by optical microscopy with a NOVEL 400. The latex solution that contained PS microspheres was spread onto a glass slide, and then covered with a cover glass. The photographs were taken at 4480× magnification. The size was measured based on the photographs.

Results and Discussions

Preparation of PS Microspheres

In the present work, monodisperse PS microspheres were prepared by a dispersion polymerization technique, which involves polymerization of styrene dissolved in an alcohol/water medium in the presence of a steric stabilizer, PVP K-30.

It is well known that the polarity of the dispersion medium has a considerably important effect on the average sizes and monodispersity of PS microspheres pre-

Table 1.
Preparation conditions of PS microspheres.[a)]

Sample	Ethanol/water	PVP K-30	IC[b)]	Sample	Isopropyl alcohol/water	PVP K-30	IC[b)]
	v/v	g/L	mol %[c)]		v/v	g/L	mol %
E-01	40/0	7.5	0.7	P-01	35/15	8.8	1.0
E-02	40/0	12.5	0.7	P-02	35/15	5.5	1.0
E-03	40/0	17.5	0.7	P-03	35/15	2.2	1.0
E-04	40/0	22.5	0.7	P-04	35/15	0.55	1.0
E-05	40/0	17.5	1.4	P-05	40/10	5.5	1.0
E-06	40/0	17.5	2.1	P-06	45/5	5.5	1.0
E-07	40/0	17.5	2.8	P-07	50/0	5.5	1.0
E-08	35/5	17.5	0.7	P-08	45/5	5.5	0.5
E-09	30/10	17.5	0.7	P-09	45/5	5.5	2.0
E-10	25/15	17.5	0.7	P-10	45/5	5.5	2.5

a) Polymerizaiton temperature: 70 °C; polymerization time: 12 h; the concentrations of styrene are 1.08 mol/L for ethanol/water and 0.87 mol/L for isopropanol/water, respectively.
b) IC: initiator concentration.
c) mol-%: mol percent of monomer amount.

pared by dispersion polymerization. Therefore, two common alcohols, namely, ethanol and isopropyl alcohol, together with water were used as the dispersion media to evaluate the effect of the polarity of dispersion medium on the PS microsphere sizes and monodispersity. Moreover, the concentration of stabilizer and initiator were also progressively changed to study their effect on the average sizes and monodispersity of PS microspheres. Preparation conditions of the PS microspheres are presented in Table 1.

Effect of Polarity of the Dispersion Medium

The polarity of the dispersion medium can be characterized by its solubility parameters. Note that ethanol and isopropyl alcohol are infinitely soluble in water, as a result, the polarity of the dispersion medium can be adjusted by changing the volume ratio of alcohol and water. The solubility parameters of water, ethanol, and isopropyl alcohol are 23.2 $(cal/cm^3)^{1/2}$, 12.7 $(cal/cm^3)^{1/2}$, and 11.5 $(cal/cm^3)^{1/2}$, respectively. The solubility parameters of the mixtures are calculated according to the following expression:[23]

$$\delta_m = (\varphi_1\delta_1^2 + \varphi_2\delta_2^2)^{1/2} \quad (1)$$

Where, φ_1 and φ_2 are the volume fractions of alcohol and water; δ_m, δ_1 and δ_2 are the solubility parameters of the mixture, alcohol, and water, respectively. According to expression (1), the solubility parameters of the alcohol/water medium are given in Table 2. The optical microscope photographs of the PS microspheres produced in ethanol/water and isopropyl alcohol/water are shown in Figure 1 and Figure 2, respectively.

Table 2.
Solubility parameters of the alcohol/water dispersion medium on average sizes and size range.

Sample	Alcohol/Water	δ_m $(cal/cm^3)^{1/2}$	Average size (μm)	Size range (μm)
E-03	40/0	12.7	2.22	MD[a)]
E-08	35/5	14.4	0.75	0.56–0.89
E-09	30/10	16	0.42	0.31–0.49
E-10	25/15	17.4	0.34	0.21–0.42
P-02	35/15	16	0.85	MD
P-05	40/10	14.7	0.71	MD
P-06	45/5	13.2	1.05	MD
P-07	50/0	11.5	0.98	0.78–1.34

a) MD: monodisperse microspheres (coefficient of variation <1.0%).

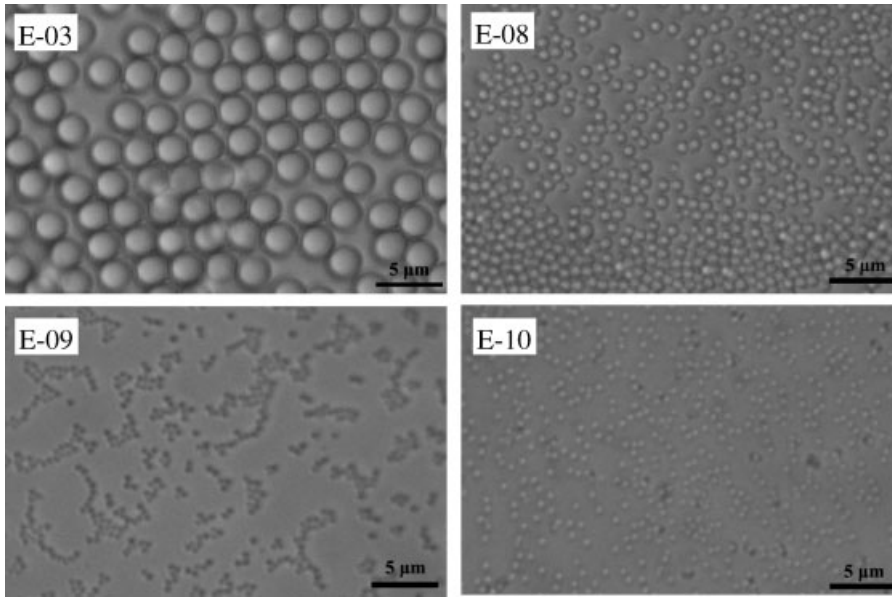

Figure 1.
Optical microscope photographs of PS microspheres prepared in ethanol/water with different volume ratios of alcohol and water. Preparation conditions of E-03, E-08, E-09 and E-10 are shown in Table 1.

As seen in Figure 1 and Figure 2, when the alcohol/water mixtures are used as the dispersion medium, there is a certain correlation between the polarity of dispersion medium and the average sizes of PS microspheres, which is further demonstrated by the data in Table 2. For the dispersion medium of ethanol/water, the

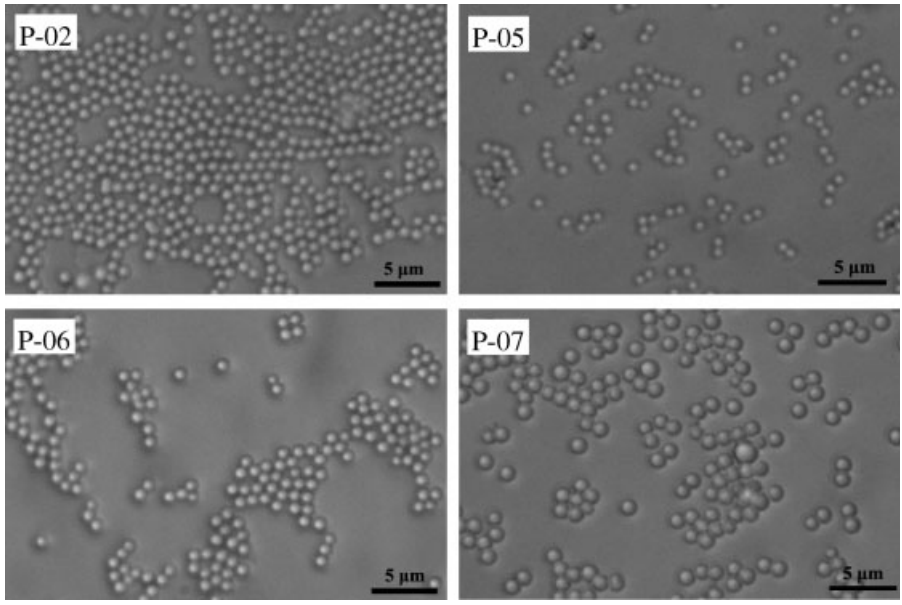

Figure 2.
Optical microscope photographs of PS microspheres prepared in isopropyl alcohol/water with different volume ratio of alcohol and water. Preparation conditions of P-02, P-05, P-06 and P-07 are shown in Table 1.

average sizes reduce with an increase in the water content of the dispersion medium, i.e., with an increase in the polarity of the dispersion medium. This is easy to understand. During polymerization, because polystyrene is non-polar, a considerably higher molecular weight of polystyrene can be dissolved in the dispersion medium with a more non-polar fraction (less water). As a consequence, PS nuclei are formed when polystyrene attains a higher molecular weight. This behavior leads to the formation of fewer nuclei and larger sizes. On the contrary, the nucleation process occurs at a lower molecular weight of polystyrene due to their reducing solubility in the dispersion medium with high water content. This effect results in the formation of more nuclei and consequently, smaller average sizes. However, for the dispersion medium of isopropyl alcohol/water, the changing trend of the average sizes is not apparent. It is not clear why such discrepancy arises between the two dispersion media, but a different monomer concentration in the mediums may account for the discrepancy.

Note that monodisperse PS microspheres can be prepared by this simple technique. Interestingly, uniform PS microspheres are only produced from ethanol without water (40/0, v/v), but the case is the opposite for isopropyl alcohol/water, in which uniform PS microspheres are only prepared from the mixed dispersion medium (35/15, 40/10, and 45/5, v/v). Moreover, isopropyl alcohol/water is the more appropraite medium to prepare monodisperse PS microspheres.

Effect of Stabilizer Concentration

In order to evaluate the effect of PVP K-30 concentration on the average sizes and monodisperisty of the PS microspheres, polymerizations were carried out in ethanol with different PVP K-30 concentrations, 7.5, 12.5, 17.5 and 22.5 g/L; and in isopropyl alcohol/water, the stabilizer concentration was 8.8, 5.5, 2.2, and 0.55 g/L, respectively. The initiator concentration and the dispersion medium remain constant. Figure 2 shows optical microscope photographs of PS microspheres produced with different PVP K-30 concentrations, and the average sizes and size range of the PS microspheres are presented in Table 3.

Table 3.
Effect of PVP K-30 concentration on average sizes and size range of PS microspheres.

Sample	PVP K-30 (g/L)	Average Size (μm)	Size Range (μm)
E-01	7.5	1.28	0.68–2.20
E-02	12.5	1.96	0.98–2.61
E-03	17.5	2.22	MD
E-04	22.5	2.31	0.98–2.68
P-01	8.8	0.52	0.41–0.62
P-02	5.5	0.85	MD
P-03	2.2	0.9	0.55–1.78
P-04	0.55	0.95	MD

As seen here, the average sizes reduce with increasing stabilizer concentration in the dispersion medium of isopropyl alcohol/water. This is due to the fact that dispersion polymerization begins and proceeds around the stabilizer chains.[24] The structure formed by the stabilizer chains in the dispersion medium can act as a skeleton for PS microsphere growth. As a consequence, increasing the number of nuclei results in more PS microspheres with a smaller size on increasing the stabilizer concentration. However, the changing trend of the average sizes is entirely the opposite for the dispersion medium of ethanol. It is difficult to explain this discrepancy, but it may due to the different polarities of the two dispersion media. Moreover, the results also indicate that monodisperse PS microspheres with different average sizes can be prepared with proper stabilizer concentration, for example, 17.5 g/L in ethanol, 5.5 and 0.55 g/L in isopropyl alcohol/water (35/15, v/v).

Effect of Initiator Concentration

The dispersion medium and stabilizer concentration were kept constant, while the initiator concentration was changed to investigate its effect on the average sizes and size range. The optical microscope photographs of PS microspheres prepared with different initiator concentrations are

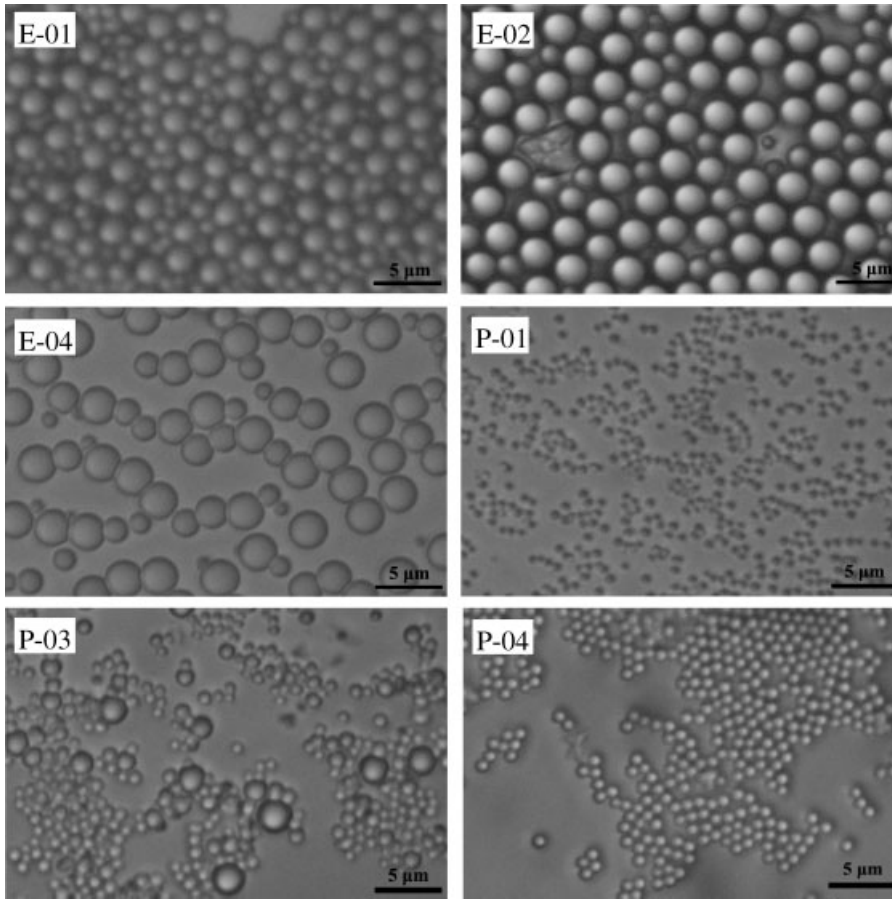

Figure 3.
Optical microscope photographs of PS microspheres prepared in ethanol and isopropyl alcohol/water (35/15, v/v) in the presence of different PVP K-30 concentration. Preparation conditions of E-01, E-02, E-04 P-01, P-03 and P-04 are given in Table 1.

given in Figure 3, and the average sizes and size range are present in Table 4.

As seen in Table 4, the average sizes do not exhibit apparent order on varying initiator concentration for the two kinds of dispersion media. Piskin et al.[17] have reported that increasing initiator concentration led to greater average size, due to the fact that lower molecular weight polymer chains are more soluble in the medium. But here, the same trend was found only with a higher initiator concentration, for example, E06 and E07, or P09 and P10. We speculated that the initiator concentration for E03 and E05, or P08 and P06, may be not high enough to reduce the molecular weight of PS and consequently, to increase the solubility of the PS chains in the dispersion medium.

More importantly, apart from the highest initiator concentration, other initiator concentrations can yield monodisperse PS

Table 4.
Effect of initiator concentration on average sizes and size range of PS microspheres.

Sample	AIBN (mol %)	Average size (μm)	Size range (μm)
E-03	0.7	2.22	MD
E-05	1.4	1.41	MD
E-06	2.1	0.81	MD
E-07	2.8	1.56	1.34–1.67
P-08	0.5	1.03	MD
P-06	1	1.05	MD
P-09	2	1.01	MD
P-10	2.5	1.16	0.98–1.45

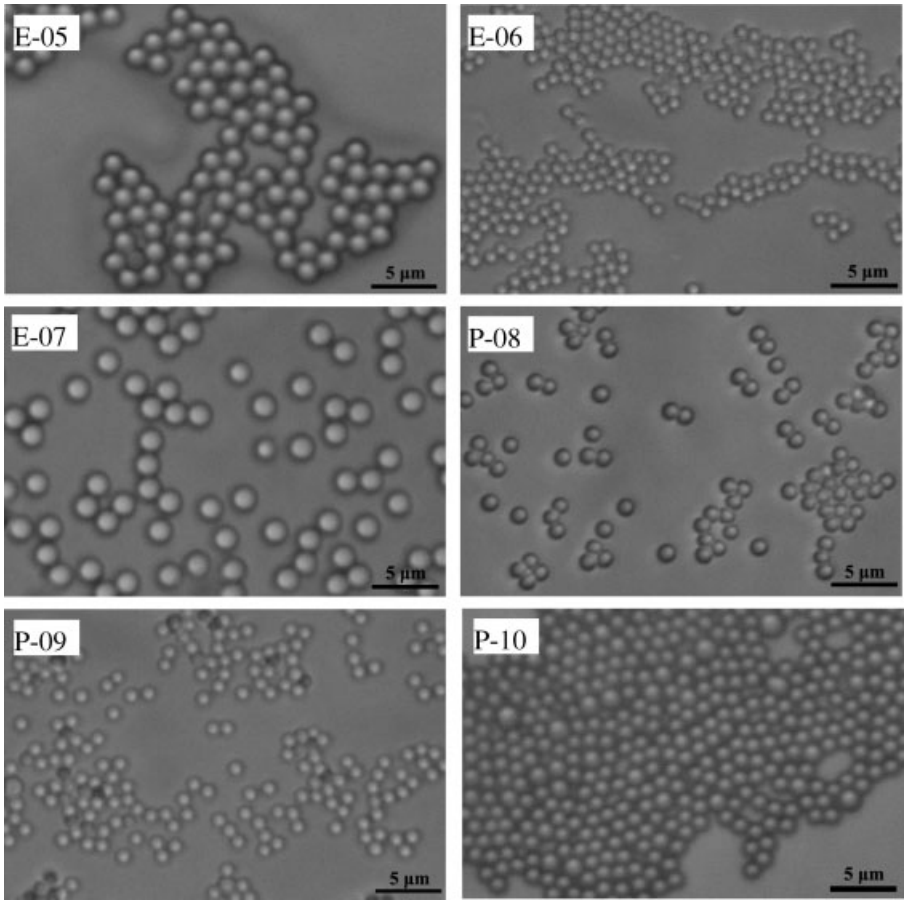

Figure 4.
Optical microscope photographs of PS microspheres prepared with different initiator concentration. Preparation conditions of E-05, E-06, E-07, P-08, P-09 and P-10 are given in Table 1.

microspheres with different average sizes in the two kinds of dispersion media. It will be helpful to prepare uniform PS microspheres by this simple and effective technique.

Conclusion

Polystyrene microspheres with different sizes were prepared by dispersion polymerization in ethanol/water and isopropyl alcohol/water media. The polarity of the dispersion medium has significant effect on the average sizes due to the solubility of the PS chains with different molecular weight. In isopropyl alcohol/water, the average sizes decreased with increasing stabilizer concentration. It can be concluded that monodisperse PS microspheres in the size range of 0.71–2.22 μm could be controllably prepared in the dispersion media of ethanol or isopropyl alcohol/water when appropriate initiator and stabilizer concentrations were employed. Furthermore, isopropyl alcohol/water is the more appropriate medium to prepare monodisperse PS microspheres.

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