Facile Size-Controllable Syntheses of Highly Monodisperse Polystyrene Nano- and Microspheres by Polyvinylpyrrolidone-Mediated Emulsifier-Free Emulsion Polymerization

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ABSTRACT: A facile emulsifier-free emulsion polymerization approach was developed to fabricate highly monodisperse polystyrene (PS) spheres using potassium persulfate as the initiator and polyvinylpyrrolidone (PVP) as a stabilizer, respectively. It was found that the size of monodisperse PS spheres tends to decrease with increase of the PVP concentration, and the size of monodisperse PS spheres could be easily controlled in a wide range from 200 to 1500 nm simply by adjusting the concentration of PVP. The increase of monomer concentration led to the increase in size of monodisperse PS spheres. In contrast, the increase of initiator concentration resulted in the decrease in size of monodisperse PS spheres. These concentration changes, however, did not significantly affect the size distributions of PS spheres. It was also found that the size of monodisperse PS spheres obtained by adding the initiator at room temperature was larger than that by adding the initiator at 70°C, and the existence of inhibitor resulted in smaller PS spheres. The mechanisms in which the above factors influence the size and size distribution were discussed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1755–1760, 2008

Key words: monodisperse spheres; polystyrene; polyvinylpyrrolidone; emulsifier-free emulsion; potassium persulfate

INTRODUCTION

Spherical polymer nano- and microspheres have received significant attention for their potential applications in drug delivery systems,[1] photonic crystals,[2–5] and as templates for other periodic structures ranging from nanometers to micrometers in size.[4–9] Among them, polystyrene (PS) nano- and microspheres are particularly interesting, and those with controlled particle morphology are the basis for many of today's advanced high-performance polymer materials, which are extensively used in a wide variety of studies.

Since Matsumoto and Ochio[10] first reported the preparation of monodisperse PS microspheres by emulsifier-free emulsion polymerization (EFEP) in 1965, based on a styrene (St)/potassium persulfate (KPS)/water (H$_2$O) system, the technique has attracted significant interest. Highly monodisperse PS spheres of narrow particle size distributions can be produced by one of the following three EFEP methods: (1) adding ionizable initiator, such as KPS; (2) adding cationic, anionic, or amphoteric surfactants[11] to the reaction system; (3) using surface-active[12,13] or amphoteric initiators.[14]

In limited literature,[15–18] the diameter of PS spheres were controlled by adding and altering the amount of polyvinylpyrrolidone (PVP) in the polymerization of styrene in hydrocarbon solvents. In contrast, to our best knowledge, there have been fewer studies of controlling the diameter of PS spheres by changing the amount of PVP in the polymerization of St in aqueous media.

In this work, we applied PVP in the EFEP of St in aqueous media, and succeeded in control of the diameter of PS spheres by altering the amount of PVP. The as-fabricated PS spheres were highly monodisperse.
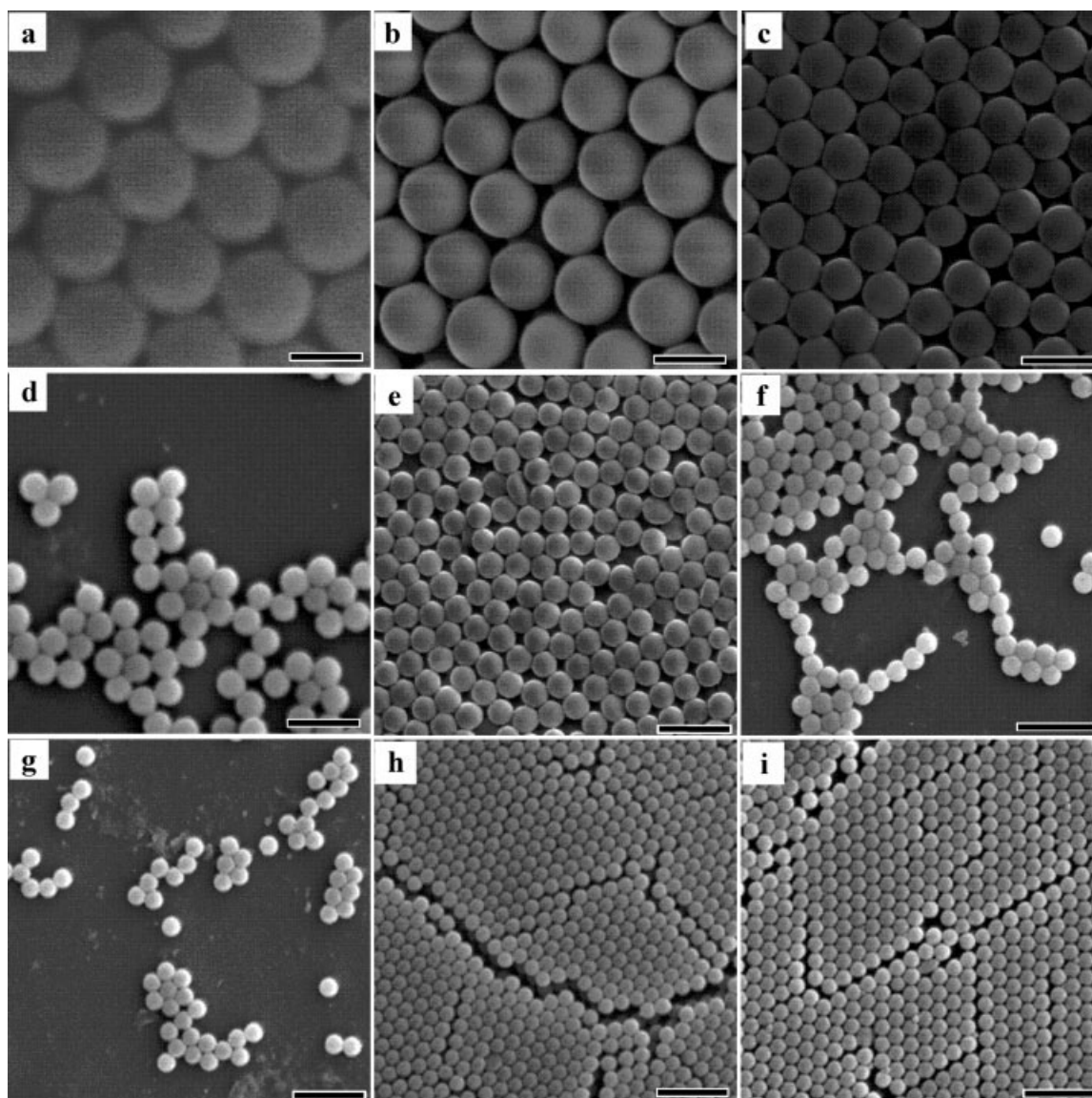
EXPERIMENTAL SECTION

Materials

Styrene (98%; Beijing Chemical Plant, Beijing, China) was purified briefly by washing (three times) with aqueous NaOH (5 wt %), followed by washing

Figure 1 SEM images of PS spheres as prepared at varied concentrations of PVP with respect to St: (a) 0 wt %, (b) 0.41 wt %, (c) 0.603 wt %, (d) 0.83 wt %, (e) 2.48 wt %, (f) 4.13 wt %, (g) 5.78 wt %, (h) 7.43 wt %, and (i) 9.08 wt % (scale bar = 1000 nm).

with pure water until neutral and drying with calcium chloride anhydrous (CaCl$_2$, Tianjin Jinke Fine Chemical Plant, Tianjin, China). KPS (Tianjin Jinke Fine Chemical Plant, Tianjin, China) and PVP ([—CH$_2$CH(NCH$_2$CH$_2$CH$_2$CO)—]$_n$, PVP, K-30, M_w ca.10,000–70,000, Xilong Chemical Plant, Shantou, China) were used without further purification. Pure water with a resistivity higher than 18.2 MΩ·cm was used in all experiments, and was obtained by a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

Preparation of polystyrene spheres

Anionic PS spheres of different diameters were prepared by EFEP using KPS as the initiator, as described previously.[12,17,19–21] Typically, under gentle magnetic stirring, 13 mL (12.1 g) of St and 0.5 g of PVP were added at room temperature to 100 mL of deionized water in a 250-mL three-neck round bottom flask in a water bath. The mixture was stirred at about 300 rpm for 15 min. After 0.3 g of KPS dissolved in 20 mL of deionized water was added, the reaction mixture was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. The mixture temperature was gradually increased to 70°C, and kept at this temperature (70 ± 3°C) for 24 h. The mixture was finally allowed to cool to room temperature. Obtained latex spheres remained suspended in their mother liquor until used. Its concentration can be adjusted by diluting the mother liquor. The residual styrene and PVP

TABLE I
Effects of the PVP Concentration on the Size and Coefficient of Variation of PS Spheres

Entry	The PVP concentration (wt %)[a]	D_n of PS spheres (nm)	C_v of PS spheres (%)	Corresponding images in Figure 1
1	0	1,415	8.3	a
2	0.41	1,001	4.1	b
3	0.603	616	4.4	c
4	0.83	417	4.1	d
5	2.48	379	4.6	e
6	4.13	283	3.8	f
7	5.78	272	3.7	g
8	7.43	245	2.7	h
9	9.08	240	2.9	i

[a] The weight percentage of PVP in terms of St monomer (12.18).

were removed by repeated washing/centrifugation/redispersing.

Characterization

A drop of the diluted emulsion was directly placed on a cover glass and dried in vacuum. Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-4300 field emission SEM. All samples were coated with a thin layer of gold by a sputter before observation. The number–average diameter (D_n) and the coefficient of variation (C_v) of particle diameter were estimated using the following equations by counting at least 50 individual particles on SEM images.

$$D_n = \left(\sum nidi \right) / \left(\sum ni \right) \quad (1)$$

$$C_v = \frac{(\sum (di - (\sum nidi / \sum ni))^2 / \sum ni)^{1/2}}{(\sum nidi / \sum ni)} \times 100 \quad (2)$$

where ni is the number of particles with a diameter of di.
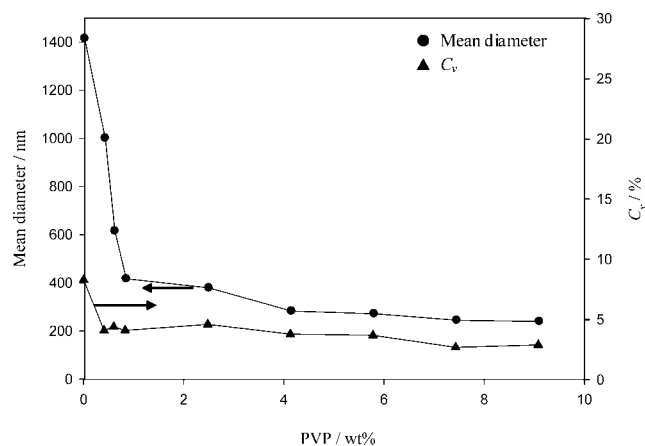
Figure 2 Dependence of the diameter (●) and coefficient of variation (▲) of PS spheres on the concentration of PVP, weight percentage of PVP is in terms of St monomer (12.1 g).

RESULTS AND DISCUSSION

Dependence of the diameter of PS spheres on PVP concentration

Effects of PVP on the size of PS spheres were studied by varying its concentration under otherwise identical conditions. The as-prepared PS spheres had neither coagulation, nor secondary particles. Figure 1 shows SEM images of PS spheres obtained at varied PVP concentrations. Clearly, all the as-prepared PS spheres were spherical and highly monodisperse, and could form closely packed assemblies. From Figure 1(a–i), the size of PS spheres decreased with increase of the PVP concentration. The largest PS spheres were obtained when no PVP was added.

More detailed analyses are summarized in Table I. While the PVP concentration varied from 0 to 9.08 wt %, the number–average diameter (D_n) and the coefficient of variation (C_v) of PS spheres changed from 1415 to 240 nm and from 8.3 to 2.9%, respectively. The latter indicated that these PS spheres were highly monodisperse.
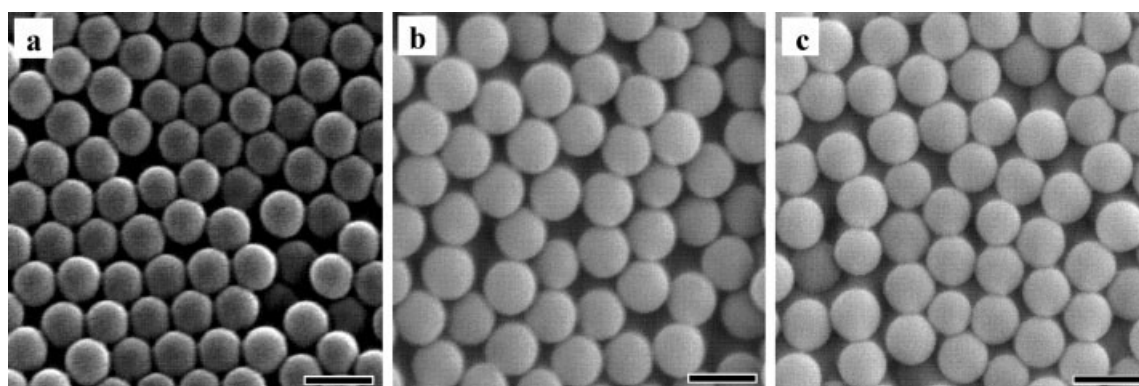
Figure 3 SEM images of PS spheres as prepared at varied concentrations of St with respect to H$_2$O: (a) 7.77 wt % (10 mL), (b) 12.43 wt % (16 mL), (c) 14.76 wt % (19 mL) (scale bar = 400 nm).

TABLE II
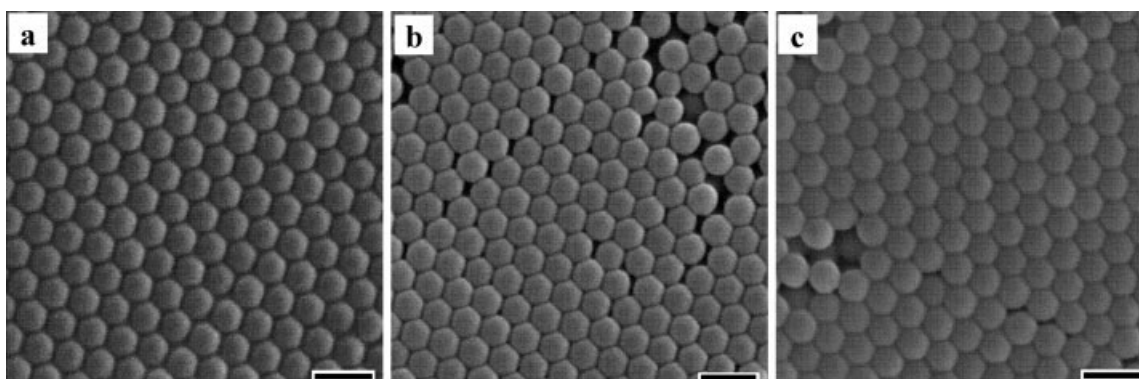**Effect of the Monomer Concentration on the Size and Coefficient of Variation of PS Spheres**

Entry	Monomer concentration (wt %)[a]	D_n of PS spheres (nm)	C_v of PS spheres (%)	Corresponding images in Figure 3
1	7.77	272	3.6	a
2	10.10	283	3.8	Figure 1(f)
3	12.43	324	3.7	b
4	14.76	375	5.0	c

[a] St concentration as weight percentage with respect to water (120 g).

Figure 4 Dependence of the mean diameter (●) and coefficient of variation (▲) of PS spheres on the St concentration, weight percentage of St is in terms of water (120 g).
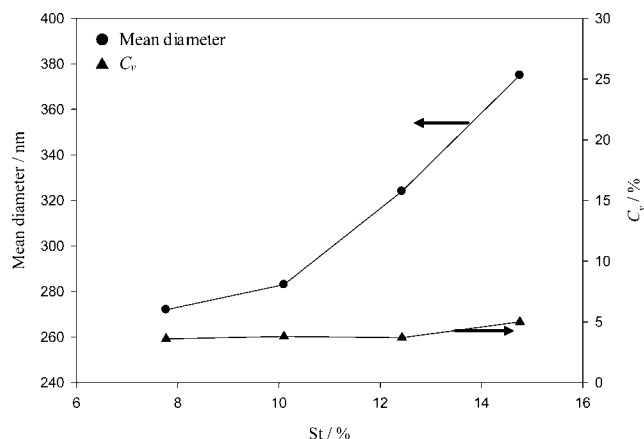
The D_n and C_v values were plotted against the PVP concentration, and the profile is shown in Figure 2. Clearly, the largest mean diameter appeared when PVP was not added. And the mean diameter decreased significantly from 1415 to 379 nm (ca. 73% decrease) with a small increase of the PVP concentration up to 2.48 wt %. Over this concentration, however, the effect of the PVP concentration was much smaller, and only a variation of D_n of 139 nm (ca. 37% decrease) was achieved over a larger variation of concentration of 6.6 wt %. The coefficient of variation C_v had slight decrease with increase of the PVP concentration.

Effect of the monomer concentration

Effect of the monomer concentration on the size and size distribution of PS spheres was investigated by varying the amount of St added. SEM images of the as-prepared PS spheres are shown in Figure 3. Their mean diameter and coefficient of variation were estimated, summarized in Table II, and plotted as a function of the St concentration (Fig. 4). Clearly, the increase of the monomer concentration resulted in small-size increase of PS spheres, and did not, however, affect their size distribution.

Effects of the initiator concentration and addition temperature

Effect of the initiator concentration on the size and size distribution of PS spheres was also investigated by varying the amount of KPS added. SEM images of the as-prepared PS spheres are shown in Figure 5. Their mean diameter and coefficient of variation were estimated, summarized in Table III, and plotted as a function of the KPS concentration (Fig. 6). Clearly, the increase of the initiator concentration resulted in the size decrease of PS spheres, and the PS spheres obtained were highly monodisperse.

It is very interesting that the addition temperature of initiator also affected the size and size distribution of PS spheres. When the initiator KPS was added at room temperature, the mean diameter and coefficient of variation of the as-prepared PS spheres were ca. 1415 nm and ca. 8.3%, respectively [see Fig. 1(a), Table I Entry 1]. When the initiator KPS was added at 70°C under otherwise identical conditions, however, the mean diameter and coefficient of variation of the as-prepared PS spheres were ca. 1034 nm and ca.

Figure 5 SEM images of PS nanospheres as prepared at varied concentrations of KPS with respect to St: (a) 1.65 wt % (0.2 g), (b) 3.30 wt % (0.4 g), (c) 4.13 wt % (0.5 g) (scale bar = 500 nm).

TABLE III
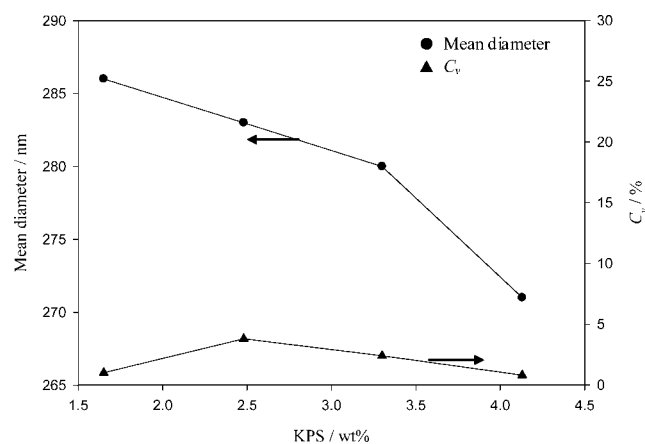**Effect of the Initiator Concentration on the Size and Coefficient of Variation of PS Spheres**

Entry	KPS concentration (wt %)[a]	D_n of PS spheres (nm)	C_v of PS spheres (%)	Corresponding images in Figure 5
1	1.65	286	1.0	a
2	2.48	283	3.8	Figure 1(f)
3	3.30	280	2.4	b
4	4.13	271	0.8	c

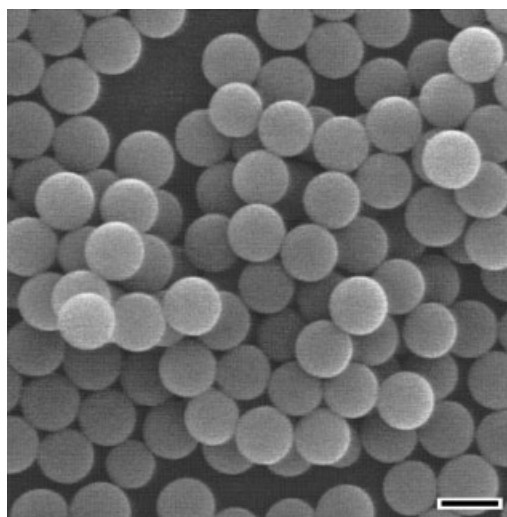[a] KPS concentration as weight percentage with respect to monomer (12.1 g).

2.1%, respectively (see Fig. 7). The decomposition temperature of KPS is higher than 60°C. Thus, when the initiator was added at 70°C, a lot of free radicals were produced in a short time. In contrast, the initiator gradually decomposed when the temperature was raised from room temperature to 70°C, and thus less free radicals were produced in the same period of time. Therefore, more primary nuclei were formed in the former case than in the latter case, resulting in smaller PS spheres and higher monodispersity.

Effect of the inhibitor

Commercial styrene usually contains an inhibitor. In this work, it was also used directly as monomer. The mean diameter and coefficient of variation of the as-prepared PS spheres were ca. 751 nm and ca. 6.0% (see Fig. 8). It was nearly half of that [1415 nm; see Fig. 1(a), Table I Entry 1] obtained using purified St. The inhibitor generally shortens the lifetime of free radicals and stops growth in size of polymer chains. Thus, the inhibitor increased the number of primary nuclei in the early stage of reaction, and thus, the mean diameter of PS spheres became smaller.

Figure 7 SEM image of PS nanospheres as prepared by adding KPS at 70°C (scale bar = 1000 nm).

Mechanism of the PVP effect

PVP is an amphiphilic polymer and is readily soluble in water and many nonaqueous solvents. This behavior arises from the presence of a highly polar amide group within its pyrrolidone ring, and apolar methylene and methine groups in the ring and along its backbone (see Chart 1). Its three-dimensional molecular structure is shown in Figure 9.[22] While the amide nitrogen is surrounded by hydrophobic methylene and methine groups, the amide oxygen is exposed, and thus free to interact with solvent molecules. An electrostatic contour map of this structure shows a significant positive potential on one side of the pyrrolidone ring due to the amide nitrogen and a significant negative potential due to the amide oxygen on the other. Since the surface of PS spheres is
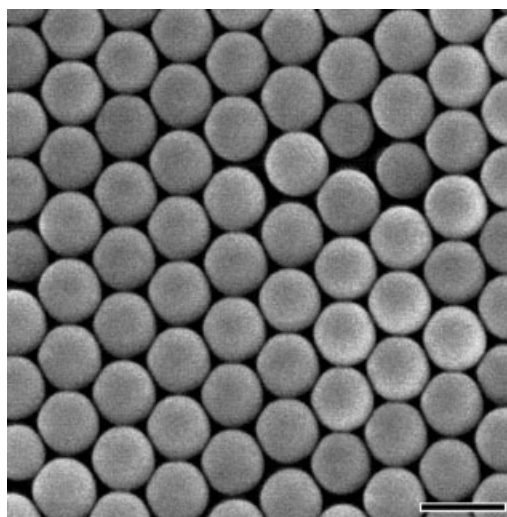

Figure 6 Dependence of the mean diameter (●) and coefficient of variation (▲) of PS spheres on the KPS concentration, weight percentage of KPS is in terms of monomer (12.1 g).
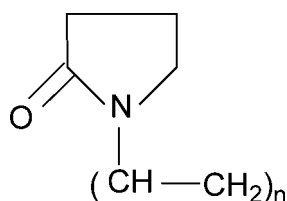

Figure 8 SEM image of PS spheres as prepared using St containing the inhibitor (scale bar = 1000 nm).
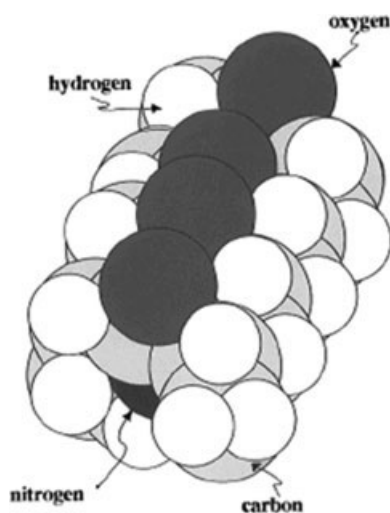
Chart 1. Chemical structure of PVP.

negative due to the presence of sulfate groups, interaction is likely to occur between these charged groups and the positive side of PVP chains. The negative dipole of the oxygen atom of the pyrrolidone ring would, however, be exposed to the aqueous environment.

In this work, PVP readily stabilizes the water/oil system during the reaction procedure, and provides colloidal stability to newly formed insoluble polymer spheres by adsorption of PVP chains on their surfaces via attractive ionic-dipole interactions, preventing further coagulation.[23] Such interactions are more than enough to bind PVP macromolecules. A higher concentration of PVP would lead to a larger number of primary nuclei (that are stabilized by PVP) in the early stage of polymerization.[18] As a result, the diameter of PS spheres tends to decrease with increase of the PVP concentration. When the PVP concentration reaches a certain value, the diameter of PS spheres no longer changes. At this stage, adsorbed PVP macromolecules quickly get saturated on the surface of nuclei at a constant monomer concentration.

CONCLUSIONS

Highly monodisperse PS spheres were readily fabricated via EFEP using KPS as the initiator and PVP as a stabilizer, respectively. As the concentration of PVP increases, the size of monodisperse PS particles tends to decrease due to an increased number of primary nuclei formed in the early stage of polymerization. Thus, the size of monodisperse PS spheres could be easily controlled in a wide range from 200 to 1500 nm by adjusting the concentration of PVP. The increase of monomer concentration led to the size increase of monodisperse PS spheres. In contrast, the increase of initiator concentration resulted in the decrease in size of monodisperse PS spheres. These concentration changes, however, did not significantly affect the size distributions of PS spheres. The size of monodisperse PS spheres obtained by adding the initiator at room temperature was larger than that obtained by adding the initiator at 70°C. The existence of inhibitor resulted in smaller PS spheres. Clearly, this work provided an easy and general approach to the preparation of monodisperse polymer spheres.

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Figure 9 Molecular structure of polyvinylpyrrolidone.