

Preparation of High Molecular Weight Monodisperse Polystyrene Latexes by Concentrated Emulsion Polymerization

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SYNOPSIS

The preparation of high molecular weight monodisperse polystyrene (PS) latexes by the concentrated emulsion polymerization is investigated. The PS latexes thus obtained have diameters in the range of 0.1–0.3 μm . The average size and the dispersity of the latexes are dependent on the concentration of surfactant (SDS), the monomer volume fraction, and the amount of nonpolymerizable additive (decane). The ionic strength does not seem to affect the size but affects the dispersity of the latexes. Under proper conditions, monodisperse particles can be prepared with a quite small standard deviation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Over the past few decades, the preparation of monodisperse polymer latexes has attracted attention because of their wide applications in chemical, physical, medical, and biological areas.^{1–5} Latexes are usually prepared by the conventional emulsion polymerization. In this method, the monomer is present in the form of droplets suspended in a medium containing both an initiator and a surfactant whose concentration is greater than the critical micelle concentration (CMC). The volume fraction of the monomer droplets is relatively small (< 0.5). This method usually produces latexes with a rather broad size distribution. Latexes with narrow size distributions have been prepared by the emulsion polymerization free of surfactant, the so-called emulsifier-free emulsion polymerization.^{6,7} The latexes thus obtained have diameters in the submicron range. Particles in the micron range have been obtained by the seeded emulsion polymerization, using either Vanderhoff's successive seeding method⁸ or Ugelstad's two-stage swelling method.⁹ The preparation of monodisperse latexes by dispersion polymeriza-

tion in organic media has also been studied.¹⁰ The molecular weights of the latexes prepared by the later method are relatively low, in the range of 10^4 – 10^6 .^{11,12} The emulsifier-free method leads to dilute latex systems and is consequently of little interest for commercial applications.¹³ The seeded methods are usually complicated.

In recent years, concentrated emulsions have been employed in this laboratory to synthesize polymers.^{14,15} The concentrated emulsion has a large volume fraction of dispersed phase (as large as 0.74–0.99) and the appearance of a gel. The dispersed phase is composed of spherical or polyhedral cells separated by thin films of the continuous phase. The shape and the size of the cells in the concentrated emulsions remain relatively unchanged during subsequent polymerization.¹⁴ Consequently, by employing the appropriate surfactant and surfactant concentration, or by changing the ionic strength and other conditions, a better control of the size and dispersion of polymer latexes becomes possible. Besides, because of the lower mobility of the monomer in each of the cells of the concentrated emulsion, the bimolecular termination step is delayed (the so-called gel effect) and high molecular weights of the latexes are expected.

In this paper, a series of experiments were conducted to prepare polystyrene (PS) latexes by the concentrated emulsion method. The dependence of

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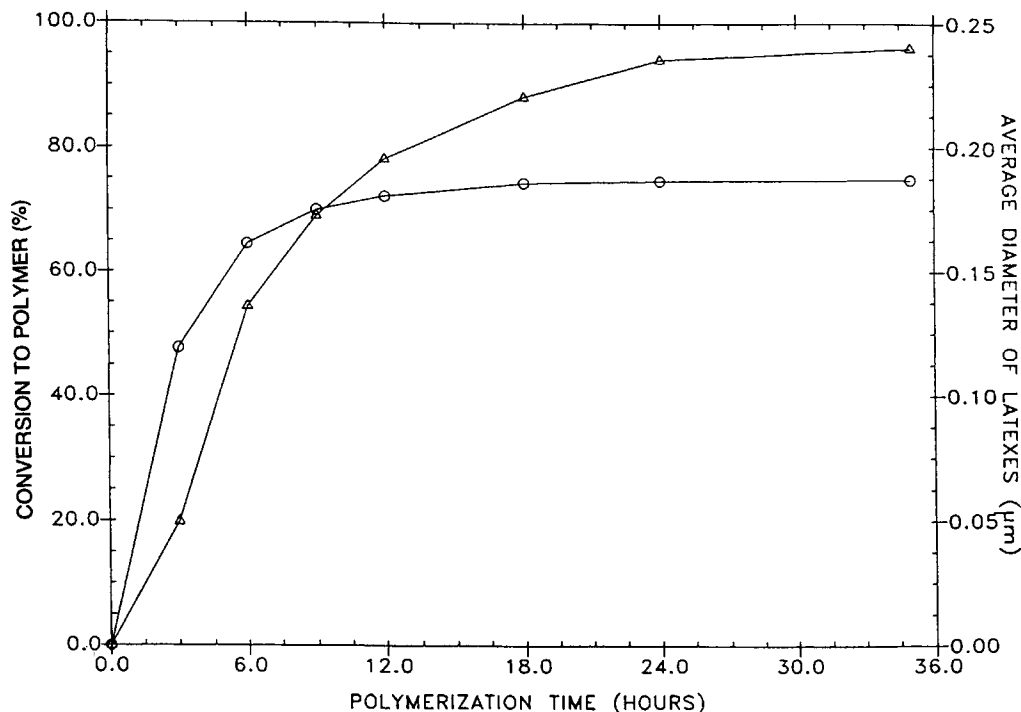


Figure 1 (Δ) Monomer conversion and (○) number average diameter of latexes against the polymerization time (50°C; [SDS] = 0.180 g/mL H₂O; Φ = 0.90).

the average particle size and dispersity on various parameters, such as polymerization time, the concentration of surfactant (SDS), the monomer volume fraction Φ, the concentration of electrolyte (NaCl), and the amount of nonpolymerizable additive (decane) present in styrene, were studied in some detail.

EXPERIMENTAL

Materials

Styrene (ST, Aldrich) was purified by distillation and azobisisobutyronitrile (AIBN, Kodak) was purified by recrystallization in methanol. Sodium dodecyl sulphate (SDS), methanol, decane, high-performance liquid chromatography (HPLC)-grade chloroform, and dichloromethane were purchased from Aldrich and used as received. Water was deionized and distilled.

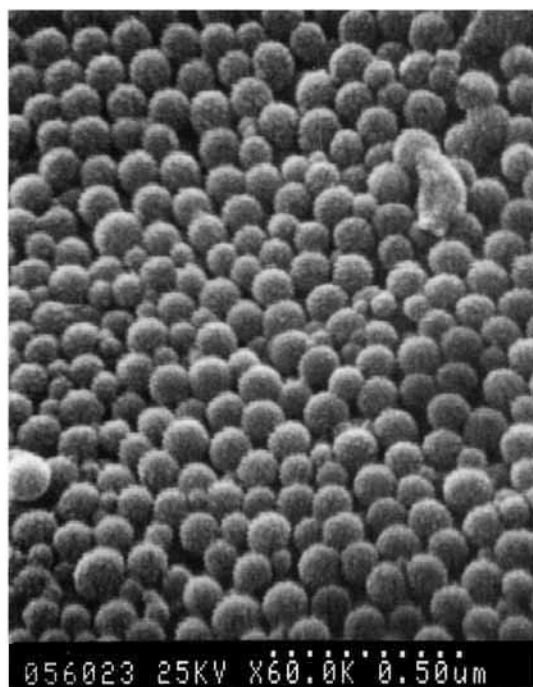
Preparation of Polystyrene Latexes

A small amount of an aqueous solution of SDS was placed in a single-neck flask of 100 mL capacity, equipped with a mechanical stirrer. Styrene con-

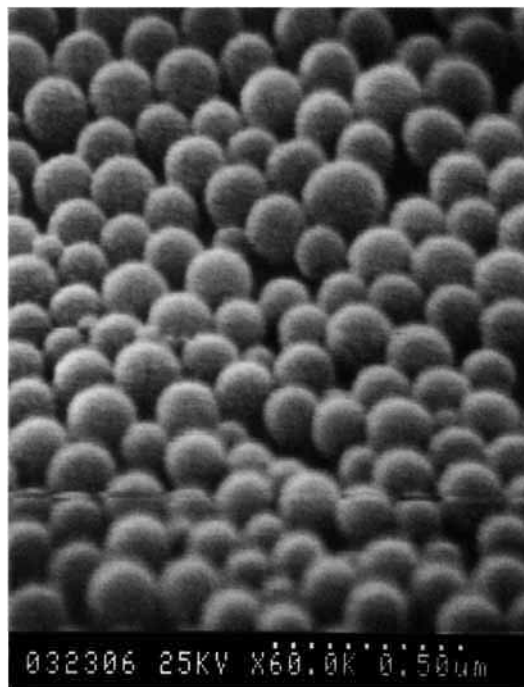
taining the initiator AIBN (0.0152 mol/L ST) was injected into the aqueous solution with a syringe, under stirring (750–800 rpm). The whole preparation process of the gel lasted 5–10 min and was conducted at room temperature. The prepared emulsion was transferred into a tube of 20 mL capacity, which was sealed with a septum. Polymerization was conducted in a temperature-controlled water bath for a certain time at 50°C.

Scanning Electron Microscopy

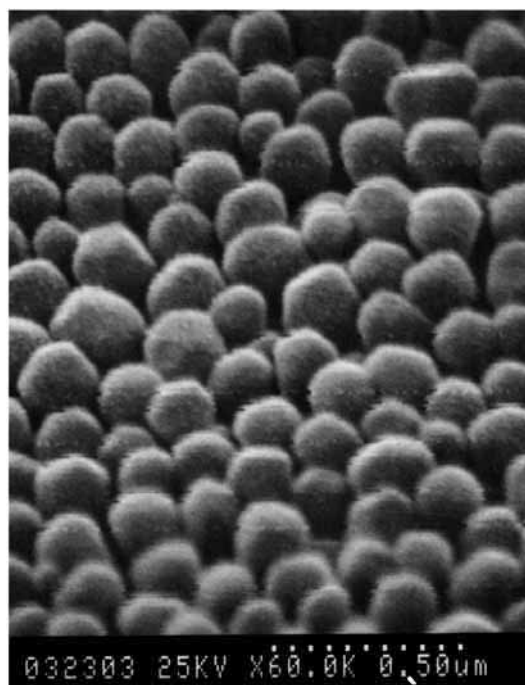
The resulting polystyrene particles were dispersed by adding water into the tube and stirring with a glass rod. After filtering to separate the aggregates and further dilution with water, a droplet of the suspension was placed onto a glass cover and dried overnight in a vacuum oven. The glass cover was mounted on SEM stubs using colloidal graphite cement. The samples were sputter-coated with a thin layer of gold in a Hexaland CT 100 Cryotrans system attached to the SEM. The prepared samples were examined with a Hitachi S-800 scanning electron microscope. The diameter of 100–150 randomly selected particles were measured for each sample, and the standard deviation was calculated.



a



b



c

Figure 2 Scanning electron micrographs of PS latexes for different polymerization times (50°C; 24 h; [SDS] = 0.180 g/mL H₂O; Φ = 0.90): (a) 3 h; (b) 9 h; (c) 24 h.

Table I Amounts Used in the Preparation of the Concentrated Emulsions^a

Dispersed phase: styrene (ST)	10.0 mL
Continuous phase: water	1.11 mL
Surfactant: sodium dodecyl sulfate (SDS)	0.200 g
Initiator: azobisisobutyronitrile (AIBN)	0.025 g

^a The concentrated emulsion was prepared at room temperature and the polymerization was conducted at 50°C for various times. In this case, the monomer volume fraction $\Phi = 0.90$, and $[\text{SDS}] = 0.180 \text{ g/mL H}_2\text{O}$.

Measurement of Polystyrene Molecular Weight and Molecular Weight Distribution

The suspension of PS latexes was poured into methanol and the precipitated PS was separated by filtration, washed with methanol in an extractor for 24 h, and dried, followed by dissolution in chloroform and finally by precipitation in methanol.

The molecular weight and molecular weight distribution was measured by employing a Waters HPLC equipment containing 500, 10⁴, 10⁵, and 10⁶ Å pore-size columns (Waters, Ultrastaygel) in a series. Dichloromethane was used as the mobile phase, and the flow rate was 1 mL/min. The detection was made by UV spectrophotometry at 254 nm. The purified and dried PS was completely dissolved in chloroform (0.1 g/L concentration) and injected into the HPLC. The HPLC was calibrated by using monodisperse PS standards (Polymer Laboratories, U.K.) of molecular weights 10⁴–12 × 10⁶.

RESULTS AND DISCUSSION

In the conventional emulsion polymerizations, radicals are absorbed into monomer-swollen micelles that are transformed into polymer particles. The monomer droplets constitute the source of the monomer. Latexes with a rather broad distribution are produced in this manner.

In the concentrated emulsions, the droplets are in the form of spherical or polyhedral cells and the continuous phase has a very low volume fraction and is in the form of a network of liquid films that separate the droplets. The adsorption of the surfactant on the surface of these droplets ensures the stability of the concentrated emulsion. Radicals, generated by the oil-soluble initiator (AIBN), transform the monomers of the cells into polymers. Since the droplets separated by the thin films are sufficiently stable, the size and shape of the latexes depend on the size of the droplets of the gel, which,

in turn, can be controlled by employing appropriate preparation conditions. Thus, a better control of the average size and size distribution becomes possible.

Figure 1 presents the polymer conversion and the corresponding latex number average diameter against the polymerization time. The scanning electron micrographs (SEM) of PS latexes for different polymerization times are presented in Figure 2. The amounts of the components used are listed in Table I. One can note that the average size grows quickly during the initial polymerization process, but remains relatively unchanged after a certain conversion to PS (about 65% conversion). The particles are narrowly dispersed, particularly at high conversions because the size of the primary cells determines the final size of the particles.

To better control the latex size and dispersity, the effects of surfactant (SDS) concentration, monomer volume fraction Φ , ionic strength (i.e., the concentration of NaCl in water), and of the amount of nonpolymerizable additive (decane) in styrene were investigated.

Effect of the Surfactant Concentration

Concentrated emulsions containing a volume fraction of ST of 0.9 with a wide range of surfactant concentrations were polymerized at 50°C for 24 h. The average particle size and dispersity of the resulting latexes are strongly affected by the surfactant concentration. The scanning electron micrographs of the corresponding latexes are presented in Figure 3. The number-average diameter and dispersity of the resulting particles are listed in Table II.

The average latex size decreases with increasing surfactant concentration because larger surface areas between the continuous and dispersed phases

Table II Effect of the Surfactant Concentration on the PS Latex Average Size and Dispersity^a

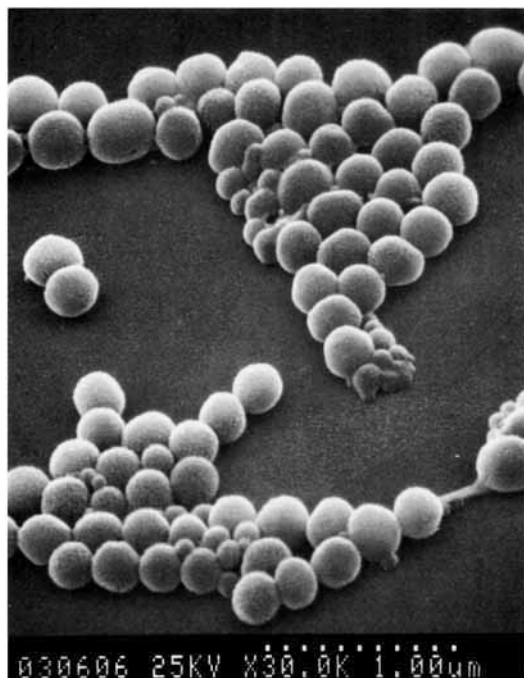
No.	[SDS] (g/mL H ₂ O)	\bar{d} (μm) ^b	SD (%) ^c
I-a	0.045	0.258	14.9
I-b	0.090	0.235	2.1
I-c	0.135	0.201	3.5
I-d	0.180	0.187	5.7
I-e	0.225	0.137	8.4
I-f ^d	0.270	—	—

^a The concentrated emulsion was prepared at room temperature and the polymerization was conducted at 50°C for 24 h; $\Phi = 0.90$.

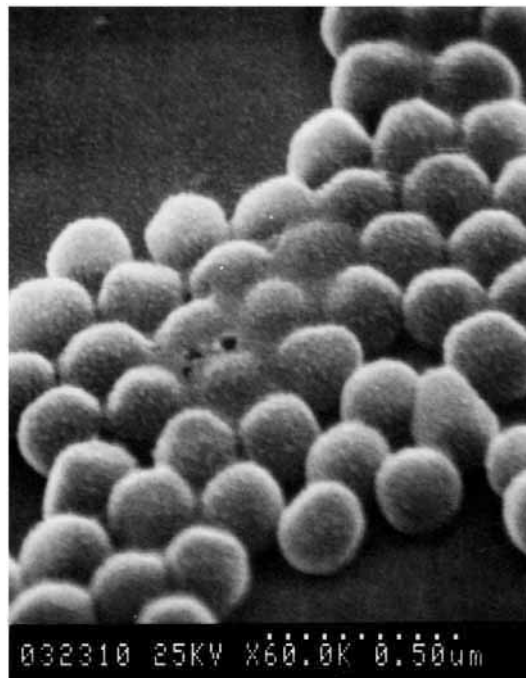
^b \bar{d} means the number-average diameter of the latex particles.

^c SD is the percent standard deviation of the mean size.

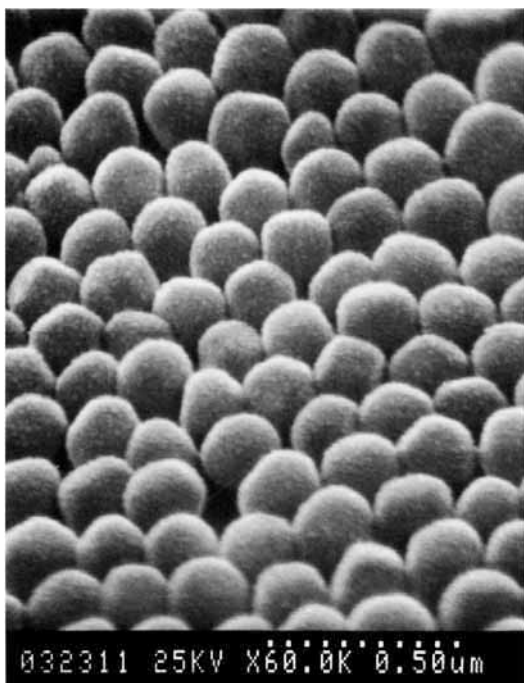
^d No gel was formed in this case.



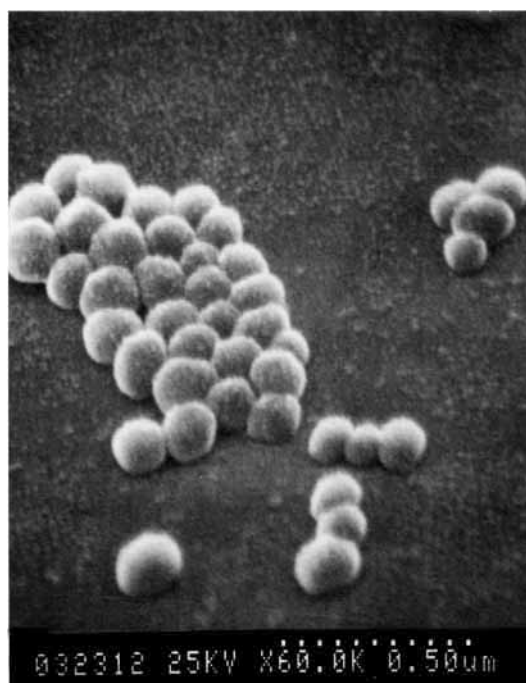
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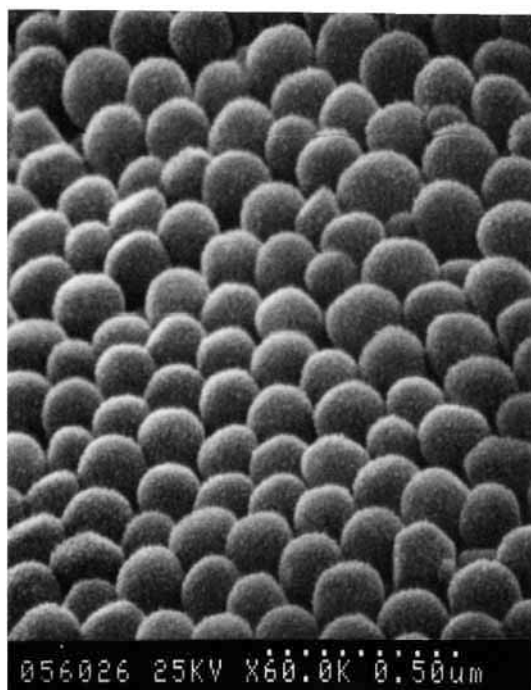


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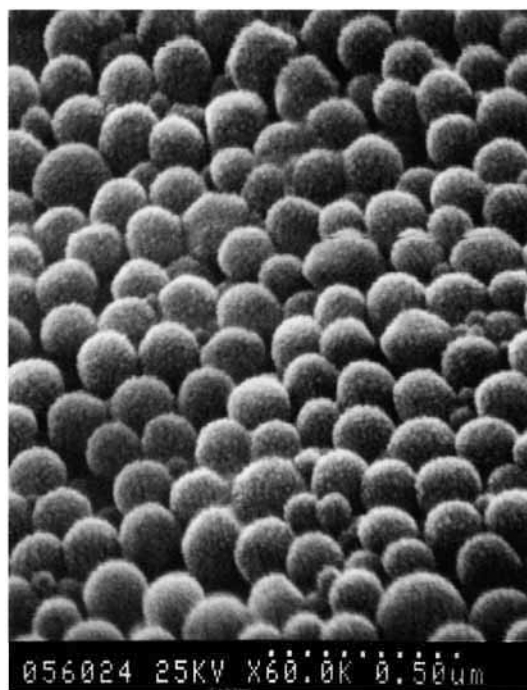


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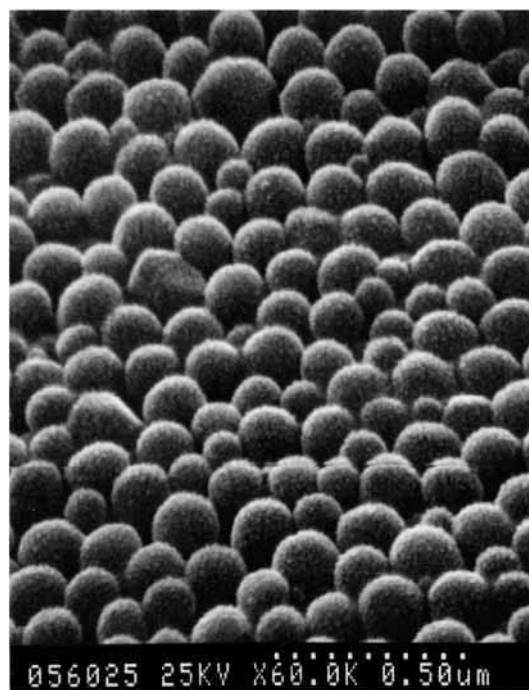
Figure 3 Scanning electron micrographs of PS latexes for different concentrations of SDS (50°C; 24 h; $\Phi = 0.90$): (a) [SDS] = 0.045 g/mL H₂O; (b) [SDS] = 0.090 g/mL H₂O; (c) [SDS] = 0.135 g/mL H₂O; (d) [SDS] = 0.225 g/mL H₂O.



a



b



c

Figure 4 Scanning electron micrographs of PS latexes for different monomer volume fractions (50°C; 24 h; [SDS] = 0.090 g/mL H₂O): (a) $\Phi = 0.85$; (b) $\Phi = 0.80$; (c) $\Phi = 0.75$.

Table III Effect of the Monomer Volume Fraction on the PS Latex Average Size and Dispersity^a

No. ^b	Φ (%)	\bar{d} (μm)	SD (%)
II-a	90	0.235	2.1
II-b	85	0.194	5.2
II-c	80	0.164	9.4
II-d	75	0.157	10.1

^a The concentrated emulsion was prepared at room temperature and the polymerization was conducted at 50°C for 24 h; [SDS] = 0.090 g/mL H₂O.

^b II-a is the same as I-b.

protected by the adsorbed surfactant become possible as the surfactant concentration increases.

One can also see that an optimum dispersity is achieved for an SDS concentration of 0.09 g/mL water. At relatively low surfactant concentrations, the repulsion between the surfaces of the films that ensures the stability of the emulsion is relatively small because the surface is not completely covered with surfactant. Coalescence of some cells can therefore occur. On the other hand, when the ionic surfactant concentration becomes too large, the

Table IV Effect of the Ionic Strength on the PS Latex Average Size and Dispersity^a

No. ^b	NaCl (M)	\bar{d} (μm)	SD (%)
III-a	0.00	0.187	5.7
III-b	0.05	0.188	5.9
III-c	0.10	0.184	8.4
III-d ^c	0.50	—	—

^a The concentrated emulsion was prepared at room temperature and the polymerization was conducted at 50°C for 24 h; Φ = 0.90; [SDS] = 0.180 g/mL H₂O.

^b III-a is the same as I-d.

^c The gel was broken during polymerization.

surface can be completely covered with surfactant molecules, but the ionic strength in the continuous phase becomes also large and this shields the electric field. As a result, the repulsion between the surfaces of the cells decreases and some cell coalescence can again occur. This explains why an optimum surfactant concentration for the dispersity exists.

Effect of the Monomer Volume Fraction Φ

Figure 4 presents scanning electron micrographs of the latexes prepared with different monomer volume

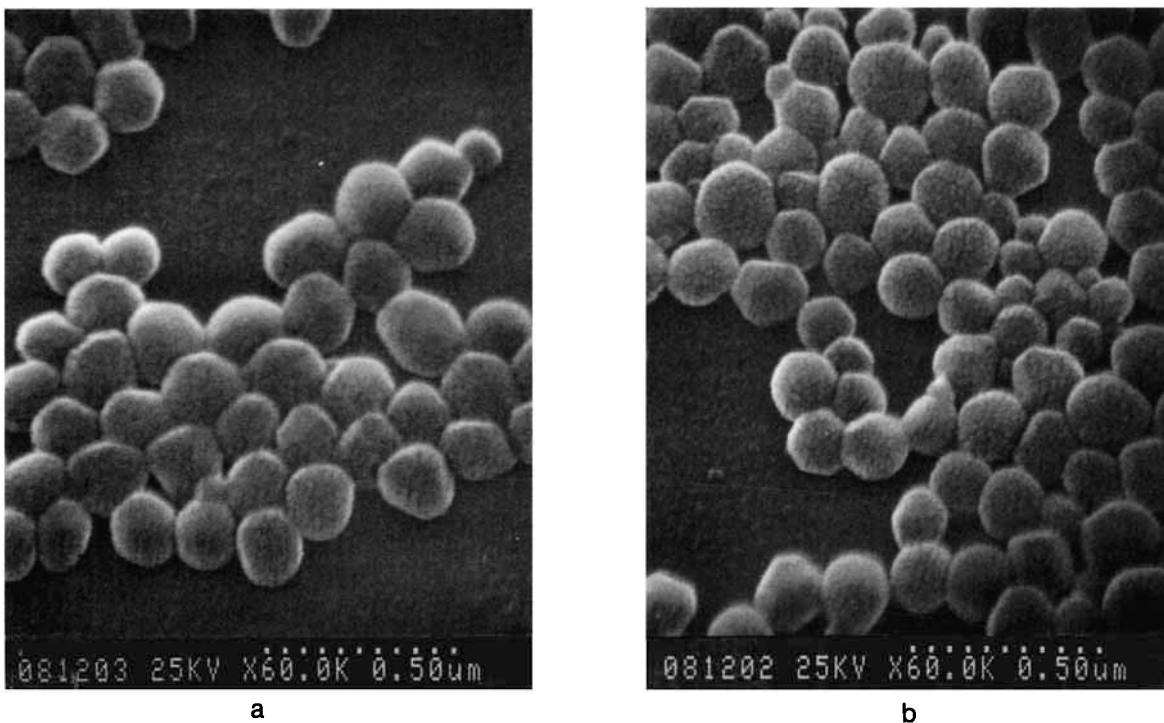
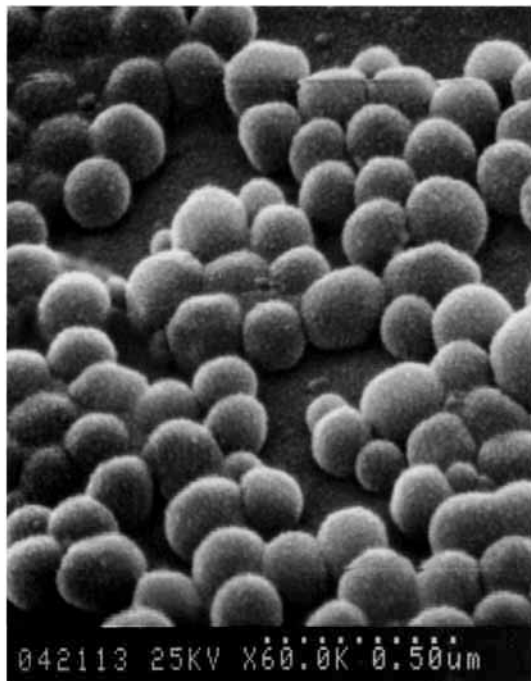
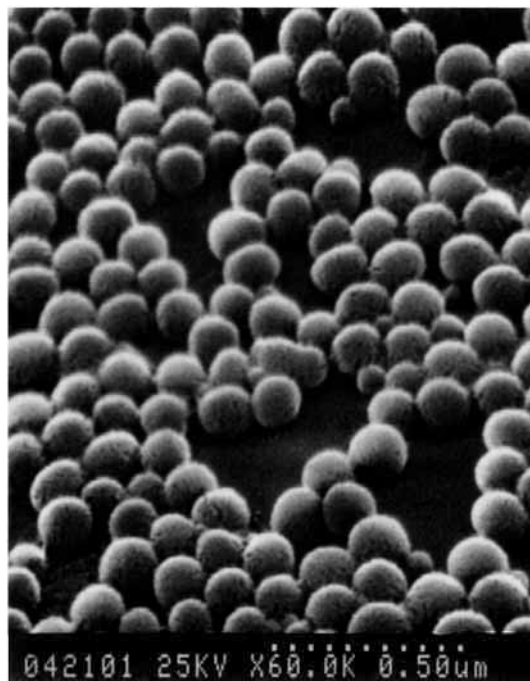


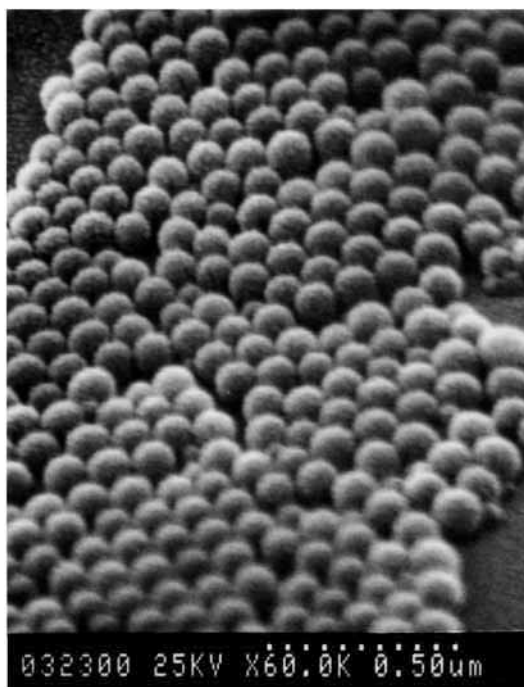
Figure 5 Scanning electron micrographs of PS latexes for different ionic strengths (50°C; 24 h; [SDS] = 0.180 g/mL H₂O; Φ = 0.90): (a) [NaCl] = 0.05M; (b) [NaCl] = 0.10M.



a



b



c

Figure 6 Scanning electron micrographs of PS latexes for different contents of nonpolymerizable additive expressed as volume ratio (50°C; 24 h; [SDS] = 0.180 g/mL H₂O; Φ = 0.90): (a) ST/decane = 85/15; (b) ST/decane = 70/30; (c) ST/decane = 50/50.

Table V Effect of the Content of Nonpolymerizable Additive on the PS Latex Average Size and Dispersity^a

No. ^b	ST/Decane	\bar{d} (μm)	SD (%)
IV-a	100/0	0.187	5.7
IV-b	85/15	0.178	6.3
IV-c	70/30	0.136	4.7
IV-d	50/50	0.106	1.8
IV-e ^c	30/70	—	—

^a The concentrated emulsion was prepared at room temperature and the polymerization was conducted at 50°C for 24 h; $\Phi = 0.90$; [SDS] = 0.180 g/mL H₂O.

^b IV-a is the same as I-d.

^c The gel remained as a gel because of the small amount of styrene.

fractions Φ and for the same surfactant concentration. The average diameter and the dispersity of the particles are listed in Table III. Comparing Figures 3(b) and 4, it is clear that the average particle size decreases when Φ decreases. This can be considered as a result of the increase in the surfactant amount when the monomer volume fraction decreases. It is worthy to note that the particle dispersity is the smallest for $\Phi = 0.9$, for reasons similar to those noted in the previous section.

Effect of the Ionic Strength

Scanning electron micrographs of PS latexes generated in the presence of various amounts of NaCl are presented in Figure 5 and the average diameter and dispersity of the corresponding latexes are listed in Table IV.

In the range of values employed, the ionic strength seems not to affect the average size but only the dispersity of the latexes, which increases as the ionic strength increases. The dispersity increases because by increasing the ionic strength the repulsion between droplets decreases and this favors their coalescence. It should be mentioned that the gel is broken when the concentration of NaCl is large enough. This occurs because of the total shielding of the electrostatic repulsion by the high ionic strength.

Effect of the Amount of a Nonpolymerizable Additive

The introduction of a certain amount of a nonpolymerizable additive, such as decane, in ST affects both the average particle size and the dispersity of the resulting latexes (Fig. 6 and Table V). The size

decreases with increasing decane content, and the particle-size distribution becomes more uniform as the content of decane increases.

The decrease of the particle size with increasing decane content may be attributed in part to the decrease in the amount of styrene involved in the polymerization in the droplets. An additional possible reason is the increased hydrophobicity of the dispersed phase, which affects the size of the cells of the concentrated emulsion. The lower dispersity may be a result of the higher hydrophobicity that ensures a higher stability of the concentrated emulsion.

Molecular Weight and Molecular Weight Distribution

The molecular weights of the resulting PS latexes are in the range of 3×10^6 to 8.5×10^6 , and the polydispersity ratio, in the range of 1.52 to 1.87.

In the concentrated emulsion, the lower mobility of the monomer in each of the cells, the so-called gel effect, leads to the delay in the bimolecular termination step. As a result, high molecular weights of the corresponding polymers are obtained.

CONCLUSIONS

High molecular weight monodisperse PS latexes can be prepared by the concentrated emulsion polymerization method. The size of the resulting PS particles is principally determined by the preparation of the precursor emulsion gels. The latter can be controlled by changing various parameters. It was found that the particle size decreases with increasing surfactant concentration, monomer volume fraction, and amount of nonpolymerizable hydrophobic additive in ST. The obtained particles are in the range of 0.1–0.3 μm . There exists an optimum surfactant concentration for which the dispersity of sizes is minimum. The dispersity is also affected by the ionic strength in water, monomer volume fraction, and content of the nonpolymerizable hydrophobic additive in ST.

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