

# Preparation of large monodisperse polystyrene particles by a one-step surfactant-free emulsion polymerization

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## LETTER TO THE EDITOR

### Preparation of Large Monodisperse Polystyrene Particles by a One Step Surfactant-Free Emulsion Polymerization

Large monodisperse polystyrene (PS) particles were prepared by one-step surfactant-free emulsion polymerization using a lower stirrer speed than applied by previous investigators. The largest PS particles prepared had a diameter of 3.2  $\mu\text{m}$ . SEM photographs showed no surface roughness on the PS particles.

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#### INTRODUCTION

Monodisperse polystyrene (PS) particles are widely used as model colloids. Aqueous PS latices are usually prepared by emulsion polymerization. The emulsion polymerization can be performed either with a surfactant or without a surfactant (soap-free or emulsifier-free).

The theory of emulsion polymerization, in which a surfactant is used, was established by Harkins (1) and by Smith and Ewart (2). The main disadvantage of the use of a surfactant is that the emulsifier is adsorbed at the interface of the PS particle and water. The removal of the adsorbed emulsifier can be quite difficult and one can never be sure that all emulsifier molecules are removed from the interface.

These drawbacks led to the development of emulsifier-free emulsion polymerization. Previous work on this subject has been reported by Matsumoto and Ochi (3), Kotera *et al.* (4, 5), and Goodwin *et al.* (6, 7).

In these polymerization systems (6, 7) monomer concentration, initiator concentration, ionic strength, and temperature have been found to be important variables. Under the conditions used it has been impossible to prepare PS latices with particle sizes larger than 1  $\mu\text{m}$  in a one-step process.

A seeded-growth procedure seemed to be a reliable way to obtain larger particles (8), but in many seeded-growth experiments new nucleation occurred and bimodal and even broader distributions were found.

Investigations on the one-step surfactant-free emulsion polymerization of styrene to obtain large PS particles (particle size larger than 1  $\mu\text{m}$ ) have, to our knowledge, never been published thus far.

In the present paper the preparation and characterization of PS particles (up to 3.2  $\mu\text{m}$ ) made by a one-step emulsion polymerization is described. Variables such as monomer concentration, initiator concentration, ionic strength, and flow pattern have been found to play a very important role. The particles obtained had a high degree of monodispersity.

#### EXPERIMENTAL

##### Materials

Water used was doubly distilled from an all-glass apparatus. The specific conductance ( $0.8 \mu\text{mho cm}^{-1}$ ) and the surface tension ( $72 \pm 0.3 \text{ mN/m}$ ) of the water indicated that it was free of surface active impurities.

Styrene was obtained from Merck (*pro analysi*, purity > 99%) and used without further purification.

Sodium chloride and potassium persulphate were obtained from Merck (*pro analysi*, purity > 99%), and used without further purification.

##### Polymerization Procedure

All polymerization reactions were carried out in 12 dm<sup>3</sup> reaction glass vessels fitted with multinecked flanged tops. Normally a reaction volume of 8500 cm<sup>3</sup> was used.

Latices with a particle size below 1  $\mu\text{m}$  were prepared in a round-bottomed reactor with four baffles (L-78) or without any baffles (L-80), using a stainless steel stirrer. Latices with particle sizes greater than 1  $\mu\text{m}$  were prepared in a flat-bottomed reactor, which is shown in Fig. 1 (all sizes in mm). The polymerization vessel had an inner diameter of 190 mm and a height of 420 mm. The vessel was provided with four baffles of stainless steel (denoted by A in Fig. 1) placed at mutual angles of 90°; every baffle had height 305 mm, depth 20 mm, and thickness 1 mm. The stirrer was of stainless steel plate (thickness 3 mm); its shape and dimensions are also shown in Fig. 1. The stirrer was operated at a height of its lowest point of 120 mm. This distance was the same for all polymerizations. The reactor was kept at constant temperature by a water thermostat bath circulating water through the double wall of the reactor.

The polymerizations were carried out in the following manner. Initially the major part of the water was added to the reactor. The stirrer and baffles were installed and care was taken to ensure that the stirrer was at the same distance from the bottom of the reactor for each polymerization.

After the reactor cover had been installed the required quantity of sodium chloride (if necessary), dissolved in 100 cm<sup>3</sup> of distilled water, was then added and washed in with a further 20 cm<sup>3</sup> of water. Then under an outflow of nitrogen the styrene was added and the stirrer was adjusted to its required speed. This speed was checked several times with a tachometer.

The mixture was then left to equilibrate for 30 min and to attain the reaction temperature to which the thermostat bath had been adjusted a few hours earlier.

After these 30 minutes the reaction was started by addition of the potassium persulphate which had been dissolved in 100 cm<sup>3</sup> distilled water at about 40°C.

The recipes for the preparation of the latices, together with relevant reaction parameters, are given in Table 1. The concentrations of all reactants are based on the aqueous phase, except the styrene percentage, which is based on the total volume.

After the reaction times mentioned the reaction mixture was cooled down to room temperature. Then the latex was filtered through a 200-mesh screen to remove any coagulum formed. Conversions were always higher than 90%.

##### Particle Size Measurements

Particle sizes of the polystyrene latices were determined with the Coulter counter (Coulter Electronics), the Coulter LS 130 (Coulter Electronics), and with scanning electron microscopy (SEM, Cambridge S 200).

##### Coulter Counter

The measurements with the Coulter counter (equipped with channel expander and 30- $\mu\text{m}$  orifice tube) are useful for particles with diameters larger than 1  $\mu\text{m}$ . In this way the particle size and the particle size distribution

TABLE 1  
Details of Latex Preparation

	Latex				
	L-78	L-80	L-86	L-88	L-89
Water (g)	7484	7725	7500	7500	7500
Styrene (g)	998	769	906	906	906
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	8.48	5.16	8.50	6.43	5.74
NaCl (g)	9.98	—	15	20	20
[Styrene] (% v/v)	12.8	9.9	11.8	11.8	11.8
[K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] (mM)	3.70	2.25	3.65	2.80	2.50
[NaCl] (M)	0.02	—	0.03	0.04	0.04
Reaction temperature (°C)	70	70	68	67	66
Reaction time (min)	290	510	960	960	960
Stirrer speed (rev/min)	300	150	160	160	160

(number, surface, and volume average) were determined. The results are given in Table 2.

### Coulter LS 130

In the particle size measurements with the Coulter LS 130 two techniques are combined; light scattering measurement (photon correlation spectroscopy) and light diffraction measurement (polarized intensity differential scattering).

With the former method particles which are much larger than the wavelength of light ( $\geq 0.8 \mu\text{m}$ ) can be measured, while the latter method is especially suitable for measuring particles that are just about the size of the wavelength (0.4–0.8  $\mu\text{m}$ ).

By this combination of measurement techniques particles in the range 0.1–10  $\mu\text{m}$  can be measured. Therefore all five latices were measured with the Coulter LS-130. The measured particle sizes are also given in Table 2.

### SEM

To obtain insight into the monodispersity and possible roughness of the particle surface, all latices were scanned by scanning electron microscopy (SEM). A drop of a dilute sample of each latex was placed onto a brass surface. The sample was then left to evaporate to dryness in a dust-free environment at room temperature. The samples were then coated with gold and scans were taken at a 90° angle. Typical SEM photographs are represented by the SEM photograph of latex L-89 in Fig. 2a.

Particle sizes and particle size distributions were determined by measuring

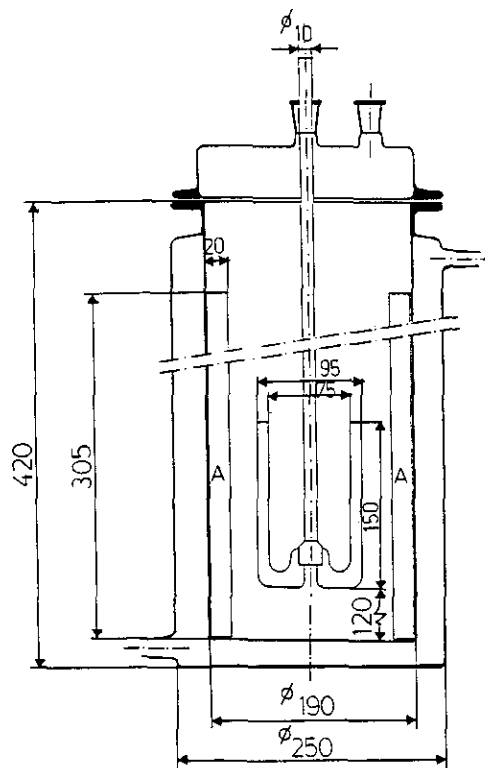


FIG. 1. Schematic drawing of the reaction vessel and the stirrer used for preparation of latices with particle diameters  $> 1 \mu\text{m}$ . Dimensions are in mm; the baffles are denoted by A.

at least 100 particles for each latex. The obtained particle sizes are also listed in Table 2.

## RESULTS AND DISCUSSION

In Table 1, the recipes for the preparation of the latices are shown. As can be seen from Table 1, a combination of factors (such as initiator concentration, ionic strength, temperature, and stirrer speed) determine the final particle size of the latices. A low reaction temperature results in the formation of fewer radicals than at a higher temperature and larger particles are obtained.

TABLE 2  
Determined Particle Sizes with Different Techniques

Latex	Coulter counter				Coulter LS 130				SEM			
	$D_n$ (nm) <sup>a</sup>	$D_s$ (nm) <sup>b</sup>	$D_v$ (nm) <sup>c</sup>	$P^d$	$D_n$ (nm) <sup>a</sup>	$D_s$ (nm) <sup>b</sup>	$D_v$ (nm) <sup>c</sup>	$P^d$	$D_n$ (nm) <sup>a</sup>	$D_s$ (nm) <sup>b</sup>	$D_v$ (nm) <sup>c</sup>	$P^d$
L-78	—	—	—	—	736	754	764	1.04	672	673	675	1.01
L-80	—	—	—	—	381	398	407	1.07	413	415	416	1.01
L-86	1309	1357	1386	1.06	1224	1247	1258	1.03	1230	1233	1235	1.01
L-88	2165	2217	2252	1.04	2018	2086	2116	1.05	1997	2001	2005	1.01
L-89	3124	3253	3279	1.02	3166	3252	3302	1.04	3086	3091	3092	1.01

<sup>a</sup> number average diameter

<sup>b</sup> surface average diameter

<sup>c</sup> volume average diameter

<sup>d</sup> degree of polydispersity ( $D_w/D_n$ )

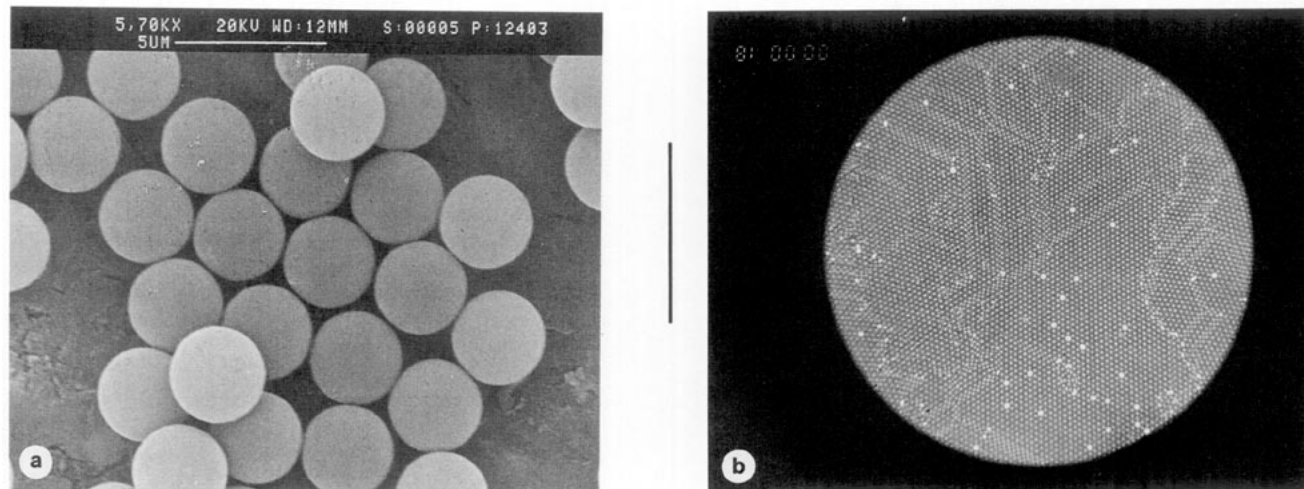


FIG. 2. Typical photographs of latex L-89 on two different scales: (a) SEM-photograph: the bar represents 5  $\mu\text{m}$ ; (b) light microscope photograph: the bar represents 100  $\mu\text{m}$ .

The fact that the monomer was used without purification (i.e., without distillation, thus without removing the inhibitor) does not seem to have any influence on the preparation of these latices.

We found that the flow pattern during the reaction (determined by the geometry of the reactor, the stirrer speed, and the type of stirrer) plays a very important role in this type of emulsion polymerization. In the present investigation, the stirrer speed was adjusted to let a styrene layer form on top of the aqueous phase, but droplets were regularly detached from the styrene layer and dispersed in the water. This is a lower stirrer speed than used by other investigators.

Particle sizes determined by various methods are listed in Table 2, where the particle sizes are listed as number average diameter ( $D_n = \sum n_i D_i / \sum n_i$ ), surface average diameter ( $D_s = \sum n_i D_i^2 / \sum n_i D_i$ ), volume average diameter  $D_v = \sum n_i D_i^3 / \sum n_i D_i^2$ , and degree of polydispersity  $P (D_v/D_n)$ , where  $n$  are the number of particles with diameter  $D$ .

As can be seen from Table 2, all the particles are monodisperse, especially the larger ones (latices L-88 and L-89). The degree of polydispersity  $P$  is always smaller than 1.07. Highly monodisperse particles have a degree of polydispersity smaller than 1.05. This is the case for latices L-86, L-88, and L-89.

Comparing the results of the measurements with the Coulter counter and the Coulter LS-130 one can see that the differences in particle size recorded by these instruments are very small. In Table 2 the results for measurements by scanning electron microscopy (SEM) are shown. The particle sizes determined are smaller (except for latex L-80) than with the other two methods, but the differences in the particle sizes are not pronounced. The fact that the particle sizes measured with SEM are smaller is explained by the fact that when the particles are exposed to an electron beam shrinkage can occur. The fact that latex L-80 as measured by SEM is larger than as measured by the Coulter LS 130 remains, however, unexplained.

In conclusion, one can say that the three methods of measuring particle sizes are very comparable, although the measuring methods are different.

In Fig. 2a a typical SEM-photograph of latex L-89 is shown. As can be seen from this picture the latex particles are spherical and monodisperse and a hexagonal packing is present. Surface roughness is not visible on the scale of the SEM photograph. The degree of monodispersity is also attested for the latices L-86, L-88, and L-89 by the large close-packed regions present. These large close-packed regions were also seen when the latices were examined under a light microscope, which is also shown for latex L-89 in Fig. 2b. Examining the latices under a light microscope reveals also the interference colours. These observations confirm that the particles are highly monodisperse.

## CONCLUSIONS

Surfactant-free emulsion polymerization is an important technique for producing PS latices. By our approach it is possible to prepare PS latices with particle sizes larger than 1  $\mu\text{m}$  in a one-step process. This method avoids some disadvantages of seeded-growth emulsion polymerization. The prepared latices are extremely useful for adsorption studies.

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