

# The Preparation of Small Polystyrene Latex Particles

W. M. BROUWER, *AKZO Corporate Research, Department of Organic and Polymer Chemistry, CRH, 6800 SB Arnhem, The Netherlands*

## Synopsis

The effects of several variables in the preparation of small-sized polystyrene latex particles are described. A semicontinuous preparation using microlatexes obtained by microemulsion polymerization as a seed is compared with a batchwise preparation employing the same ingredients. The particles in the batch products prove to be slightly larger in size but are more narrowly distributed. Furthermore, the effects of both the surfactant type and the ionic strength on the particle size in the batchwise emulsion polymerization of styrene are reported. The systems do not obey the linear Smith-Ewart relationship with respect to the micellar surfactant concentration, although in the microemulsion polymerization of styrene the Smith-Ewart relationship is found to be valid with respect to the initiator concentration. Surfactants with a low critical micelle concentration increasingly promote the formation of smaller particle sizes. Salt is found to decrease the particle size when using a strong adsorbing surfactant. However, in the case of a weak adsorbing surfactant, an increase in particle size has been observed above a certain salt concentration.

## INTRODUCTION

Monodisperse polymer colloids, i.e., latexes, in the submicron size range are easily obtained by emulsion polymerization. Using an ionic initiator, e.g., sodium persulfate, stable latexes may be obtained in the presence of surfactants.<sup>1</sup> In the latter case generally larger particle sizes are obtained. The preparation of very small latex particles (i.e., 10–100 nm) has for several reasons not been described extensively. Small particles are often not as monodisperse as the larger-sized latex particles, since the nucleation stage is relatively long as compared with the growth stage in the process of preparation. Moreover, the particles are difficult to separate from the continuous phase and not easy to characterize.

In this article attention is focused on the preparation of small-sized, narrowly distributed, polystyrene latexes. Although thermodynamically stable microemulsions with droplets in the 1–10 nm size range have been known for a long time,<sup>2</sup> few investigations on the polymerization of styrene microemulsions have been reported so far.<sup>3–6</sup> Polymerization of these microemulsions might yield very small-sized latex particles if the droplets are effectively initiated. Recent results obtained with the polymerization of the larger sized droplets in miniemulsions of styrene support this assumption.<sup>7</sup>

In this article the preparation of polystyrene microlatexes, using a cationic and an anionic surfactant and *n*-pentanol and *n*-hexanol as costabilizers, is reported. These microlatexes were then used as a seed for further emulsion

polymerization and the results were compared with those of a batchwise preparation. Furthermore, the effectiveness of several surfactants ranging in critical micelle concentration from  $5 \times 10^{-2}$  to  $5 \times 10^{-5}$  mol/L was investigated, as well as the effect of salt in the batchwise preparation of small-sized polystyrene latex particles. Mostly azobisisobutyronitrile was used as the initiator and in some instances also sodium persulfate. The results may be of both practical and theoretical interest.

## EXPERIMENTAL

### Reagents

All surfactants obtained were of reagent grade. Sodium dodecyl sulfate (SDS, Janssen), sodium decanesulfonate (Janssen), and hexadecyl (cetyl) trimethylammonium bromide (CTAB, Merck) were used as supplied. All fatty acid soaps were prepared by neutralizing the fatty acids (Janssen) stoichiometrically with standardized solutions of alkali. Sodium sulfonate succinic acid dialkyl esters (Aerosol MA-80 and Aerosol OT-75 with an alkyl chain of 1,3-dimethylbutyl and *n*-octyl, respectively) were obtained from American Cyanamid and first dried by evaporating the water/isopropanol mixture in which they had been dissolved. *n*-Pentanol and *n*-hexanol were reagent grade and obtained from Baker.

Styrene (Janssen) was washed with 5% w/w aqueous solution of potassium hydroxide in order to remove the inhibitor and subsequently washed with demineralized, distilled water, until the wash water reacted neutrally. Finally, the monomer solution was dried on anhydrous calcium chloride. Azobisisobutyronitrile (AIBN, Janssen) or sodium persulfate (Baker) was used as thermally decomposing initiator.

Distilled demineralized water was used throughout the polymerization experiments.

### Preparation of the Microemulsions

Surfactant (potassium palmitate or cetyltrimethylammonium bromide), *n*-alkyl alcohol, and styrene were weighed in a conical flask and mixed by magnetic stirring. Subsequently, water was added in portions, while stirring. Upon heating the closed container slightly, the turbid emulsion suddenly transformed into a clear, transparent microemulsion after a few minutes. Table I shows the recipes.

### Preparation of Microlatexes

The styrene in water microemulsions (see Table I) were heated to 80°C in a stirred reactor equipped with a condenser (stirring speed 250 rpm) and initiated by adding a concentrated solution of AIBN in acetone (0.94 g in 3 g acetone) using a syringe. Upon adding the initiator solution, the reaction mixture became turbid and transparent again after a few seconds. This turbidity is possibly due to evaporation of the acetone leaving solid AIBN in the reaction solution. The AIBN is very quickly taken up by micelles or styrene droplets so that the mixture becomes transparent again.

TABLE I  
Recipes for Styrene/Water Microemulsions

Designation	Surfactant		<i>n</i> -Alkyl alcohol		Styrene	Water
	C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br	C <sub>15</sub> COOK	<i>n</i> -C <sub>5</sub> OH	<i>n</i> -C <sub>6</sub> OH		
ACI 1	10 <sup>a</sup> (0.055)			5 (0.098)	10 (0.198)	500
ACI 4		15 (0.102)		5 (0.098)	10 (0.198)	500
AAJ 58	20 (0.110)		10 (0.227)		20 (0.396)	500

<sup>a</sup>In grams; between brackets molar concentration based on water.

After some time, the transparent reacting solution started becoming bluish due to the formation of polystyrene microparticles. In some cases the microlatexes thus formed were used as seeds for further emulsion polymerization of styrene. Next, 50 min after initiating the original microemulsion, 65 g of styrene containing 0.38 g AIBN was added in 165 min by means of a peristaltic action pump.

### Batchwise Preparation of Latexes

In the batchwise preparation of polystyrene latexes, using AIBN as the initiator, surfactants, and water (500 g) were fed to the reactor and heated to 80°C followed by the addition of styrene (75 g). The mixture was then stirred at 500 rpm for 5 min and at 250 rpm for 10 min, and subsequently initiated using 1.32 g AIBN in 4.2 g acetone.

The preparations using sodium persulfate were slightly different. Here 8.4 g of the surfactant (Aerosol MA) was mixed with 600 -  $x$  ( $x < 100$ ) g of water and heated to reaction temperature. Then 300 g styrene was added and stirred at 400 rpm. In order to prevent thermal polymerization<sup>8</sup> after 5 min, the reaction was started by the addition of a solution of sodium persulfate and sodium bicarbonate (molar ratio = 1 : 3.4) in  $x$  mL water. Thus the aqueous phase contained 36 mM Aerosol MA.

### Particle Size Analysis

Latex particle size was measured by quasielastic light scattering, using a Malvern 4700 zeta sizer setup. The particle size could be measured very reproducibly  $\pm 2$  nm for particle sizes between 20 and 80 nm.

As a qualitative indicator of the particle size distribution a polydispersity index (PDI) was obtained from the scattered intensities. PDI values smaller than 0.1 were indicative of fairly monodisperse samples, as verified with calibration latexes.

### Molecular Weight Analysis

Polymer molecular weight was analyzed with the aid of size exclusion chromatography, using a PL-mix column (Polymer Laboratories, U.K.) and a calibration curve obtained by eluting monodisperse polystyrene samples. The eluent was tetrahydrofuran.

## RESULTS AND DISCUSSION

## Microemulsion Formation and Polymerization

From Table I it is apparent that the dispersed styrene phase in the microemulsions does not exceed 4% w/w (AAJ 58). This was experienced to be a maximum using the surfactant contents as indicated. Similar phase ratios were observed by Atik and Thomas<sup>3</sup> and Johnson and Gulari,<sup>6</sup> who prepared microemulsions with cetyltrimethylammonium bromide and hexanol, and sodium lauryl sulfate and pentanol, respectively. It is known that o/w microemulsions are not likely to reach the dispersed phase content of w/o microemulsions, since the ionic surfactants used favor the formation of w/o emulsions.<sup>9</sup>

Nevertheless, using a combination of nonionic and anionic stabilizers (Pluronic and Aerosol MA) a 30% w/w styrene/brine microemulsions has been prepared, but the system coagulated during polymerization.<sup>5</sup>

In classical emulsion polymerization theory it is believed that the number of micelles determines the amount of nuclei and thus the final particle size.<sup>10</sup> More recently, Dunn and Al-Shahib<sup>11</sup> showed that not the number but the surface area of the micelles is the dominating factor. However, in miniemulsion polymerization,<sup>7</sup> where the monomer droplets are smaller (0.1–0.5  $\mu\text{m}$ ), droplet initiation seems to compete with a micellar nucleation mechanism. In the present microemulsions, the droplets must be very small ( $< 10$  nm), since the mixtures are completely transparent, and a vast amount of them may start to polymerize when enough initiator is present.

In Table II the particle number density after microemulsion polymerization of AAJ 58 is listed as a function of the initiator (AIBN) concentration. Evidently, the particle size drops, i.e., the particle number increases considerably with increasing the initiator concentration. However, the smallest size obtained with an initiator concentration at 26 mM is 21 nm, which is still many times larger than the initial microemulsion droplets. This means that during microemulsion polymerization droplets coalesce or particles coagulate, whereas monomer transport from smaller to larger droplets is likely to occur due to the Kelvin–Thompson effect as soon as the interfacial tension attains a positive value.

Striking is that the microemulsion polymerization system seems to obey the Smith–Ewart relationship for emulsion polymerization, originally described for the emulsion polymerization of water insoluble monomers (like styrene)

TABLE II  
Effect of Initiator Concentration on Particle Size and Size Distribution in the  
Microemulsion Polymerization of Styrene

Designation	[I] (M)	Diameter DLS (nm)	PDI <sup>a</sup>
AAJ 61 <sup>b</sup>	0.0264	21	0.45
AAJ 62 <sup>b</sup>	0.0085	28	0.18
AAJ 63 <sup>b</sup>	0.0026	37	0.11

<sup>a</sup>PDI = polydispersity index, obtained from dynamic lightscattering

<sup>b</sup>The microemulsion formulation is identical with that of AAJ 58, Table I.

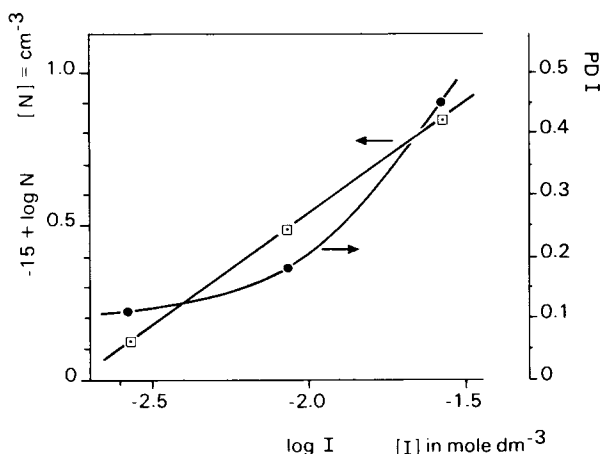


Fig. 1. Particle number density  $N$  and polydispersity index PDI as a function of the initiator concentration (AIBN) in the polymerization of styrene microemulsions (AAJ 58, Table 1). Temperature is  $80^{\circ}\text{C}$ .

and aqueous phase initiation in the presence of micelles:

$$\log N = K + n \log a_s + n \log S + m \log I \quad (1)$$

where  $N$  = particle number density,  $K$  = a constant, indicative of the efficiency of radical entry in particles,  $S$  = micellar surfactant concentration,  $I$  = initiator concentration, and  $a_s$  = the surface area of a surfactant molecule on the latex particle; the coefficients  $n$  and  $m$  were theoretically shown to range between 0.4 and 0.6.

In the present case we observe  $m = 0.73$  (see Fig. 1), which does not much deviate from the theoretical value. Figure 1 also indicates that the polydispersity drops when the particles grow bigger. Evidently, the growth stage of the larger particles exceeded that of the smaller ones.

### Seeded vs. Batchwise Polymerization

The styrene/water microemulsions composed of CTAB or potassium palmitate and *n*-hexanol (see Table 1, ACI 1 and ACI 4) were used after polymerization as seeds for further styrene emulsion polymerization. Thus 65 g of styrene, containing 0.38 g AIBN, was added continuously to these microlatexes over a period of 165 min. The final diameter, polydispersity factor, and weight average molecular weight were compared with those obtained by a batchwise preparation, using the same ingredients: 75 g styrene and 1.32 g AIBN added at the start. For comparison, also batchwise preparations were conducted in the absence of *n*-hexanol.

Table III shows the results. It turns out that the microlatex-seeded emulsion polymerization yields smaller particles than the batchwise preparation in the presence of *n*-hexanol. Yet, particle size distribution remains broad in the seeded product, whereas the batchwise products are fairly monodisperse. A reason for the smaller seeded products may be found in a more efficient use of the surfactants employed. As the amount of styrene present in the microemul-

TABLE III  
Particle Size, Polydispersity Index, and Molecular Weight for Seeded and Batchwise Emulsion Polymerization of Styrene

Designation	Diameter (nm)				PDI				$10^{-5} M_w$ (g mol <sup>-1</sup> )			
	Seed <sup>a</sup>		Batch		Seeded		Batch		Seed		Batch	
	H	Seeded <sup>b</sup> H	H <sup>c</sup>	— <sup>d</sup>	H	Seeded H	H	—	H	Seeded H	H	—
C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br	26	51	62	59 ± 2	0.27	0.27	0.09	±0.02	3.6	2.1	6.0	±0.2
C <sub>15</sub> COOK	25	40	53	52	0.17	0.19	0.07	0.05	2.4	0.9	2.4	5.1

<sup>a</sup> For recipes see table I; initiator (AIBN) concentration is 0.94 g in 525 mL microemulsion.

<sup>b</sup> To 10 g polystyrene in the seed; 65 g styrene is added semicontinuously.

<sup>c</sup> Recipes corresponding with those of the seed have been used, but with 75 g styrene instead of 10 g in the original recipe (Table I).

<sup>d</sup> See <sup>c</sup> but *n*-hexanol is absent.

sion is lower than that in the batch emulsion, the number of nuclei that can be stabilized will be larger in the seed latex. Consequently, the final particle size in the seeded product will be smaller than in the batch product. Moreover, the increase in diameter of the seeded product using CTAB ( $d = 2.0d_{\text{seed}}$ ) coincides with that calculated from the increase in volume ( $d = 7.5^{1/3}d_{\text{seed}} = 2.0d_{\text{seed}}$ ), assuming that no additional crop of particles is formed. In the case of potassium palmitate the smaller size of the seeded product may indicate the formation of a second crop of particles, which in turn may be caused by the larger amount of surfactant present (see Table I).

Finally, the presence of *n*-hexanol does not significantly affect the particle size or distribution in the batch products (see Table III). Though essential in the formation of microemulsions, *n*-hexanol does not contribute to an overall stabilization of the latex particles. Instead, a retardation of reaction rate was observed due to radical transfer to the alcohol, as indicated by the lower molecular weight of the hexanol containing products. In conclusion, batchwise preparation of small-sized polystyrene latex particles yields a higher monodispersity than the seeded preparation using the polydisperse seed microlatexes. However, the particle size is larger for the batch products.

#### Effect of Surfactant on Particle Size in Batchwise Preparation

Equation (1) describes the Harkins–Smith–Ewart relationship between the particle number density after the nucleation stage on the one hand and the initiator as well as the micellar surfactant concentration on the other for a micellar nucleation mechanism.

The surfactant concentration should exceed the critical micelle concentration (cmc) and the monomers should be virtually insoluble in water, like styrene. Provided that no partial particle flocculation occurs,  $N$  in eq. (1) may equal the number density at complete conversion. For styrene a coefficient  $m = 0.55$  was found previously.<sup>12</sup> However, in many emulsion polymerization systems a homogeneous nucleation mechanism was shown to be operable,<sup>13</sup> since considerable deviations from the theoretical coefficient in eq. (1) were observed, often depending on the type of initiator employed.

For the batchwise preparation of small-sized polystyrene latex particles, the Smith–Ewart relationship was checked, using various surfactants ranging in critical micelle concentration from 0.05 to  $5 \times 10^{-5}M$ . The initiator concentration (AIBN) was fixed at 0.0186*M* and the surfactant concentration based on the water phase was 0.102*M*. The variable micellar concentration  $S$  was calculated from this value and the cmc values given in Table IV. The results are shown in Figure 2.

Interestingly, not a straight but a curved relationship is observed between  $\log N$  and  $\log S$ , which indicates that surfactants with a low cmc become much more efficient in producing small particle size than anticipated according to the Smith–Ewart relationship. All ionic surfactants used, widely varying in type and structure, fit the curve. Although most surfactants possess a similar value for  $\alpha_s$ —around  $50 \text{ \AA}^2$  on polystyrene latices of intermediate surface charge density,<sup>14-16</sup> as calculated from the saturation adsorption on hydrophobic polystyrene latexes—Aerosol OT was reported to occupy a much larger surface area  $\alpha_s = 100 \text{ \AA}^2$ .<sup>15</sup>

TABLE IV  
Particle Size and Polydispersity Index of Polystyrene Latexes Prepared Batchwise Using Different Surfactants<sup>a</sup>

Designation	Surfactant				Latex	
	Surfactant name	<i>T</i> (°C)	CMC ( <i>M</i> )	Ref. <sup>b</sup>	Size, DLS (nm)	PDI
1	Sodium undecanoate	—	0.05	16	79	0.10
2	Sodium decanesulfate	40	0.043	16	78	0.14
3	Aerosol MA	60	0.048	19	79	0.07
4	Sodium dodecanoate	25	0.025	16	69	0.10
5	Sodium tridecanoate	25	0.013	16	57	0.12
6	Sodium dodecylsulfate (SDS)	—	0.0081	20	62	0.07
7	SDS/0.02 <i>M</i> NaCl	—	0.0038	20	61	0.06
8	SDS/0.1 <i>M</i> NaCl	—	0.0014	20	56	0.10
9	Aerosol OT	15	0.002	16	55	0.11
10	Potassium hexadecanoate	35	0.0017	16	52	0.05
11	SDS/0.4 <i>M</i> NaCl	—	0.0005	20	51	0.04
12	Hexadecyltrimethyl ammonium bromide	60	0.0012	21	48	0.11

<sup>a</sup>Total surfactant concentration is 0.102*M*; 75 g styrene was used in 500 g water. Initiator (AIBN) concentration is 0.0186*M*. Temperature is 80°C.

<sup>b</sup>Reference to literature.



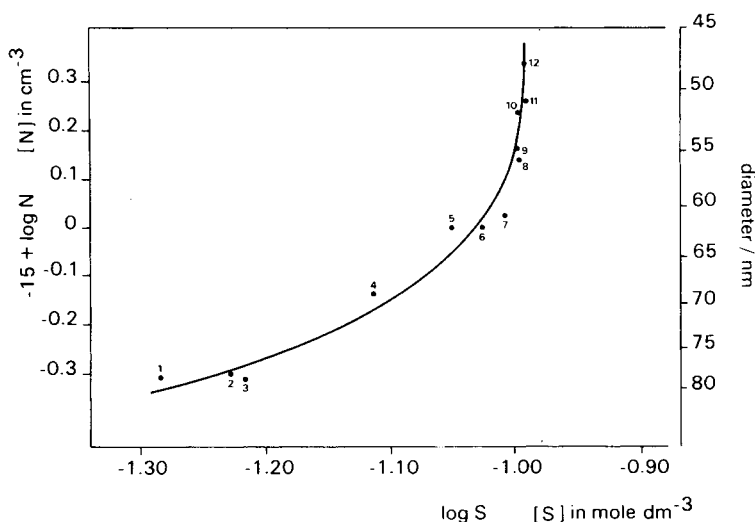


Fig. 2. Double logarithmic plot of particle number density  $N$  and micellar surfactant concentration  $S$  for the batchwise emulsion polymerization of styrene. Surfactant concentration is  $0.102M$ . Initiator (AIBN) concentration is  $0.0186M$ . Styrene concentration is  $75\text{ g}/500\text{ g water}$ . Temperature is  $80^\circ\text{C}$ . (1) Sodium undecanoate; (2) sodium decanesulfonate; (3) Aerosol MA; (4) sodium dodecanoate (laurate); (5) sodium tridecanoate; (6) sodium dodecyl (lauryl) sulfate (SDS); (7) SDS/ $0.02M$  NaCl; (8) SDS/ $0.1M$  NaCl; (9) Aerosol OT; (10) potassium hexadecanoate (palmitate); (11) SDS/ $0.4M$  NaCl; (12) hexadecyl (cetyl) trimethylammonium bromide.

Nevertheless, the result obtained with the latter surfactant also fits the curve. This would suggest that the value  $\alpha_s$  is not a determining parameter in the relationship between particle number and surfactant concentration in the present system.

The particle size distribution did not seem to vary significantly over the range of cmc values (Table IV) within the error of measurement. However, recently Feeney et al.<sup>17</sup> have shown that in the emulsion polymerization of styrene, Aerosol MA yields latexes of higher monodispersity than surfactants like Aerosol OT and sodium dodecylsulfate due to a larger radical entry rate after the nucleation stage when Aerosol MA is used. The polydispersity index, obtained from light-scattering data, is probably not sensitive enough for the detection of small differences in polydispersity. Nevertheless, their conclusion that a coagulation mechanism underlies the polystyrene latex particle formation is in agreement with the nonlinearity of the curve in Figure 2.

Furthermore, the use of a nonionic surfactant, a nonyl phenol ether of polyoxyethylene with 10 ethyleneoxide repeating units ( $\text{cmc} = 5 \times 10^{-5}M$ ), did not result in the formation of very small particles, but instead yielded nonporous microbeads in the size range of  $1\text{--}3\text{ }\mu\text{m}$ , which is unusually large for a one step suspension polymerization. This result can be explained from the dissolution of the nonionic surfactant in the styrene phase,<sup>18</sup> thus matching the density of the dispersed phase with the aqueous medium and reducing the emulsifying power tremendously. As a result, some of the surfactant was included in the beads, which gave rise to the turbid appearance of the beads.

### Effect of Ionic Strength on Particle Size in Batchwise Preparation

The presence of small amounts of salt lowers the critical micelle concentration of ionic surfactants significantly and may be used to decrease particle size at a fixed surfactant concentration. On the other hand, high levels of salt may also effect an increase of particle size, due to flocculation caused by surfactant charge shielding, i.e., compression of the electrical double layer. The effect of salt (sodium chloride) on particle size was investigated for a relatively strong (sodium lauryl sulfate) and a weakly adsorbing emulsifier (Aerosol MA)<sup>15</sup> in the batchwise polymerization of styrene, using AIBN as the initiator. Figure 3 shows the results. For both emulsifiers it is found that particle size drops at increasing concentrations of salt in the lower salt concentration region; however, for the weakly adsorbing emulsifier the particle size increases at higher ionic strength. In the case of sodium lauryl sulfate, however, the particle size decreases even at 0.4M sodium chloride. For Aerosol MA also a minimum is obtained for the particle number density as a function of the ionic initiator concentration (sodium persulfate) at a fixed initiator-to-sodium bicarbonate ratio of 0.3 on molar basis (see Fig. 4). By increasing the initiator concentration and thus the ionic strength, the particle number density initially increases but at initiator concentrations higher than  $2 \times 10^{-2}M$  particle

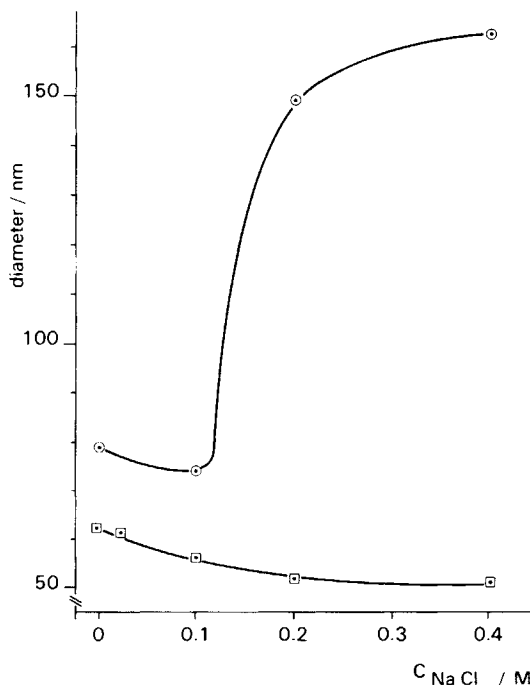


Fig. 3. Particle size vs. sodium chloride concentration in the batchwise emulsion polymerization of styrene using different surfactants: (○) Aerosol MA; (□) sodium dodecylsulfate. Surfactant concentration is 0.102M and initiator (AIBN) concentration is 0.0186M. Styrene concentration is 75 g/500 g water; temperature is 80°C.

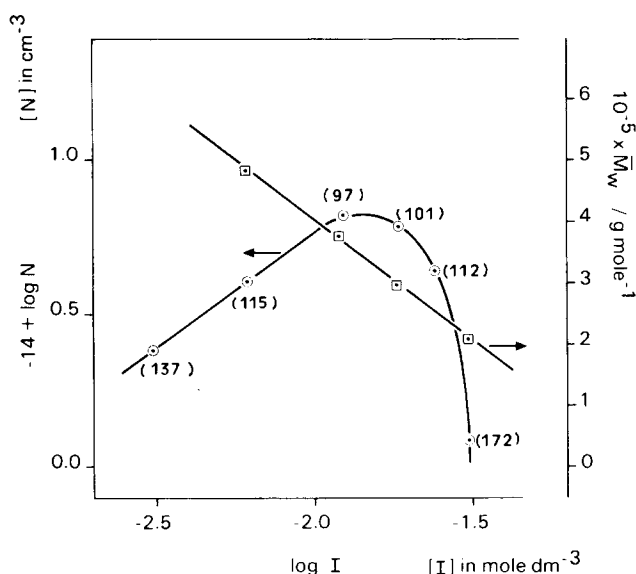


Fig. 4. Particle number density and weight average molecular weight as a function of the sodium persulfate concentration in the batchwise emulsion polymerization of styrene; 300 g/600 g water. Aerosol MA was used as the surfactant (36 mM based on water). Sodium bicarbonate was used as the buffer. Buffer to initiator ratio is 3.4 on molar mass basis. Temperature is 70°C. Particle diameter between brackets.

number density drops rapidly. As expected, the molecular weight decreases with increasing initiator concentration.

So, ionic strength may be a useful tool for reducing the particle size in the presence of strong, well-adsorbing surfactants, especially when the latex is post-cleaned to remove superfluous additives.

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