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ORIGINAL CONTRIBUTION

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"Emulsifier-free" emulsion copolymerization of styrene and butylacrylate: particle size control with synthesis parameters

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Abstract This paper presents the synthesis of film-forming particles with controlled diameters. The copolymerization of styrene and butylacrylate is realized by emulsion synthesis in the presence of potassium sulfopropylmethacrylate (SPM), an ionogenic monomer and sodium bicarbonate. The initiator, ammonium persulfate, and the SPM ensure the stabilization of particles. After the particles are washed, their diameters are measured by Dynamic Light Scattering (DLS) with a Zetasizer 3 (Malvern). The particle diameters are controlled by SPM concentration and the ionic strength of the medium. An increase of ionic strength, at constant [SPM], increases diameters, though an increase of [SPM], at constant ionic strength, decreases diameters. The experimental results are interpreted by two different modelizations, either by log–log equations like in the literature, or by semi-log and exponential equations. The latter ones give better modelization.

Key words Emulsion polymerization – control of particle diameters – ionogenic monomer – poly(styrene-co-butylacrylate) – film-forming latexes

Introduction

Emulsion polymerization has been largely developed to elaborate lattices with narrow size distribution, since the pioneer work of Vanderhoff et al. [1] in 1970. Especially, a lot of studies have been done upon particle size control of polystyrene lattices.

Ottewill et al. [2, 3], for instance, and also Krieger et al. [4, 5] wrote a lot of papers on the subject. The mainly used method is emulsion polymerization of styrene without surfactant.

Ottewill et al. [2, 3] showed that it is possible to obtain polystyrene particles with variable diameters and narrow diameter distributions by controlling experimental parameters such as polymerization absolute temperature T (K), monomer [M] (mol/l) and initiator [P] (mol/l) concentrations, and ionic strength I (mol/l).

The influences of these parameters have been summarized in empirical relations:

$$\log D_{\mathrm{nm}} = 0.238\left[\log \frac{I\ [\mathrm{M}]^{0.23}}{[\mathrm{P}]} + \frac{4929}{T}\right] - 0.827 \qquad (1)$$

for anionic initiator $K_2S_2O_8$ [2], and

$$\log D_{\mathrm{nm}} = 0.384\left[\log \frac{I\ [\mathrm{M}]^{1.099}}{[\mathrm{P}]^{0.833}} + \frac{2563}{T}\right] - 0.195 \qquad (2)$$

for a cationic initiator ABA.2HCl (Azobis-isobutyramidine chlorhydrate) [3].

Particle diameters are increased from 40 to 1100 nm either by an increase of ionic strength or monomer concentration, or by a decrease of polymerization temperature or initiator concentration.

Krieger et al. [4, 5] used similar systems, but introduced an anionic [4] or cationic comonomer [5]. The authors obtained the same results as Ottewill, and showed that ionic comonomers acted as a surfactant. An increase of comonomer concentration decreased particle diameters. For the anionic system [4], they also obtained an empirical relation

$$D_{\text{Å}} = 166 \times \left(\frac{[\text{NaSS}]}{[I]}\right)^{-0.64} \times [\text{A}]^{-0.20} \times [\text{M}]^{0.46} \qquad (3)$$

with diameter varying from 149 to 350 nm.

About emulsion copolymerization of styrene and butylacrylate, we found only few papers, mainly on kinetic studies [6–11]. Among them, there were two papers of Pichot et al. [10, 11] who studied the emulsion copolymerization of styrene and butylacrylate first in the presence of an ionogenic comonomer, potassium sulfopropylmethacrylate (SPM), and second in the presence of a polymerizable surfactant, sodium acrylamido undecanoate (AUNa). The authors just indicated the particle sizes they obtained.

In this paper, we synthesize latex particles by the same way as Pichot et al. [7], and we study the influence of two parameters, ionogenic comonomer (SPM) concentration and ionic strength, upon particle diameters.

Experimental

Reagents

Styrene (Sty) (>99%) (104.15 g/mol) and butylacrylate (Abu) (>99%) (128.17 g/mol) were purchased by Janssen. Potassium sulfopropylmethacrylate (SPM) (98%) (246.33 g/mol), ammonium persulfate $(NH_4)_2S_2O_8$ (98%) (228.19 g/mol) and sodium bicarbonate $NaHCO_3$ (99%) (84.01 g/mol) were purchased by Aldrich. All reagents were used as received. Fresh distilled water was used every time.

Polymerization

All polymerization reactions were carried out in a 1 l double-jacket glass flask. First, Sty (0.37 mol/l), Abu (0.33 mol/l), SPM (variable) and sodium bicarbonate (variable) are stirred at 450 rpm, heated and purged under nitrogen in the reactor until the polymerization temperature was reached. Then, the initiator (3×10^{-3} mol/l), dissolved in minimum water, was introduced. The polymerization was carried out at 70 °C for 15 h.

Washing

Washing is necessary to remove all the ions dissolved in water.

The latex suspensions are washed either by contact with ion-exchange resins (MB5101 Rohm and Haas, mix of a cationic and an anionic resin) or by successive centrifugations (20 000 rpm at 2 °C) until conductivity of latex suspensions is lower than 500 μS/cm.

Characterization of particle sizes

The particle diameters are measured by Dynamic Light Scattering by using a Zetasizer 3 of Malvern. The measurements are realized before and after washing. Generally, the diameters are bigger after washing, because of the extension of the electric double layer due to decrease of ionic strength.

Results

Preliminary study

First, we studied the influence of the variation of ionic comonomer concentration as method of Pichot et al. [10]. Results are presented in Fig. 1.

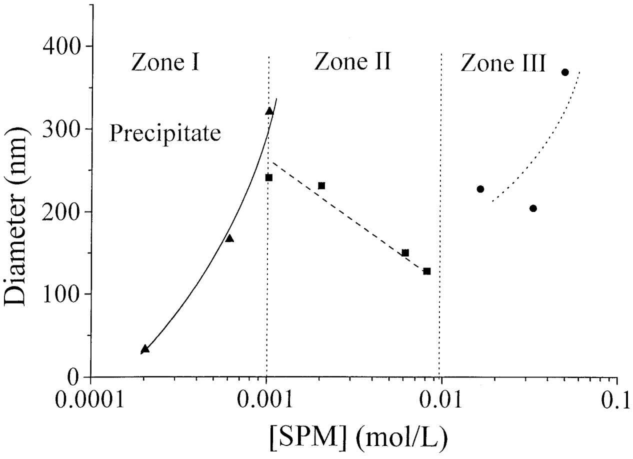
This figure shows three zones with different behaviours of particle diameters with [SPM]:

In the second zone, $0.001 \leq [\text{SPM}] \leq 0.01$ mol/l, we observed the same influence as classical surfactant: the particle diameters decrease when [SPM] increases.

But in zones 1 and 3, we observed the inverse behaviour: particle diameters increase when [SPM] decreases.

In the first zone, when [SPM] is very small, (≤ 0.001 mol/l), the diameters are very small. This phenomena is in fact due to an important formation of precipitate during the synthesis, which can reach more than

Fig. 1 Variation of particle diameter versus the log of SPM concentration $[NaHCO_3] = 5.71 \times 10^{-3}$ mol/l, $[\text{Sty}] = 0.37$ mol/l, $[\text{Abu}] = 0.32$ mol/l, $[(NH_4)_2S_2O_8] = 2.98 \times 10^{-3}$ mol/l



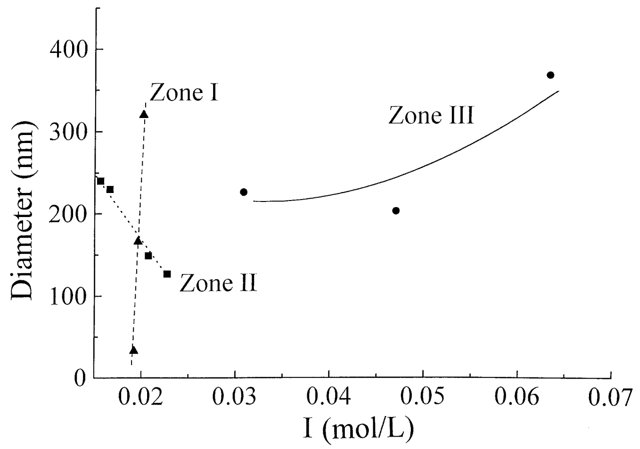


Fig. 2 Variation of particle diameters with ionic strength $[NaHCO_3] = 5.71 \times 10^{-3}$ mol/l, [Sty] = 0.37 mol/l, [Abu] = 0.32 mol/l, $[(NH_4)_2S_2O_8] = 2.98 \times 10^{-3}$ mol/l

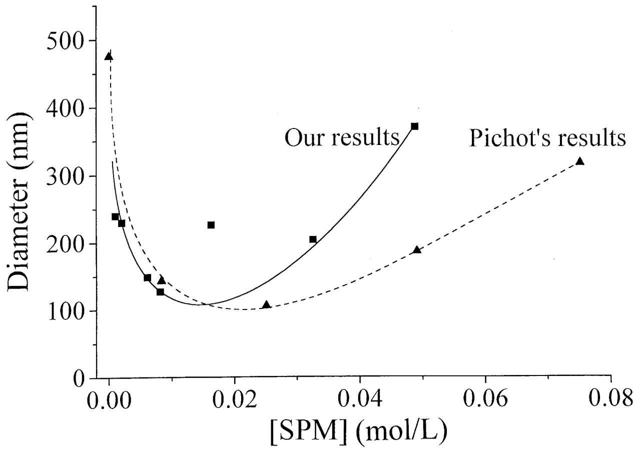


Fig. 3 Comparison of Pichot's results with our results (same experimental conditions, except for the agitation rate which is not indicated by Pichot) (from [10])

50% by weight of the initial charge of monomers. The measurement is made in fact only on stabilized particles, which are very small and very few because of the very small SPM concentration. When [SPM] increases, the stabilization is improved, the stabilized particles are bigger and more numerous and the precipitate is less important. So the mean diameter increases with [SPM].

In the third zone, [SPM] ≥ 0.1 mol/l, we observed an increase of diameters, whereas [SPM] increases too. This inversion of variation, in comparison with the second zone, is better understood if we consider the variation of the ionic strength in Fig. 2: we can see easily that for high [SPM], the ionic strength is much increased.

It is important to note that in this third zone, the particles are well stabilized. The SPM molecules linked covalently to the particles are probably more numerous in this zone than in zones 1 and 2. So the variation of diameters with [SPM] is similar to that one with ionic strength observed by Ottewill.

Increasing [SPM], leading to bringing the particles closer, leads to depletion of hydrosoluble polymers of SPM. Stabilization is then ensured by electrostatic repulsion of the electric charges linked covalently to the particles.

If we interpret Pichot's results [10] in term of particle diameter variations, we observe quite similar variations, appearing on Fig. 3: for low concentrations, the diameters decrease, though for higher concentrations, they increase with an increase of SPM concentration. The small differences which can be observed are probably due to different experimental conditions. The agitation rate, for instance, not indicated by Pichot et al., may be very important.

Systematic study: control of particle diameters

Second time, the aim of this work was to synthesize different particles in the largest panel of diameters. According to the literature and our first results, it is evident that, to obtain small particles, the ionic strength should be small, and the SPM concentration high, and to obtain big particles, the ionic strength should be high, and SPM concentration small.

To avoid having the same phenomena as in the preliminary work, we studied independently ionic strength and SPM concentration. So we varied

- either SPM concentration at constant ionic strength *I*,
- or ionic strength *I* at constant [SPM].

In each case, the ionic strength was adjusted with $NaHCO_3$.

For SPM, we chose four concentrations which were equal or higher than the low critical value 10^{-3}mol/l: 32.5×10^{-3}, 8.1×10^{-3}, 4.1×10^{-3} and 0.8×10^{-3} mol/l.

For the ionic strength *I*, we chose three values which were quite high to obtain big particles: 4.7×10^{-2}, 7.05×10^{-2} and 9.4×10^{-2} mol/l.

The experimental conditions and the results are presented in Table 1.

The results were analysed by two different ways:

- the same way as Ottewill and Krieger,
- another way which better interprets our results.

Classical analysis as Ottewill and Krieger

First, the results were analysed by representing the variation of particle diameters versus either the SPM

Table 1 Variation of particle diameters for different ionic strength and SPM concentration

[SPM] [mol/l]	$I = 4.7 \times 10^{-2}$ mol/l	$I = 7.05 \times 10^{-2}$ mol/l	$I = 9.4 \times 10^{-2}$ mol/l
32.5×10^{-3}	103.4 nm	156.0 nm	172.5 nm
8.1×10^{-3}	245.8 nm	319.4 nm	403.0 nm
4.1×10^{-3}	268.6 nm	338.1 nm	507.1 nm
0.8×10^{-3}	505.1 nm	546.0 nm	850.0 nm

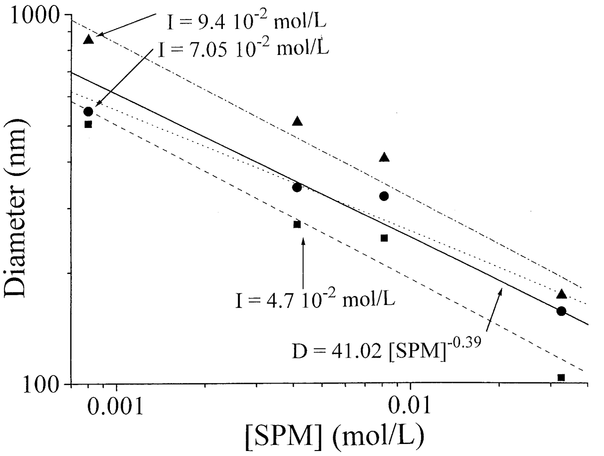


Fig. 4 Log–log representation of variation of particle diameters with [SPM] at constant ionic strength

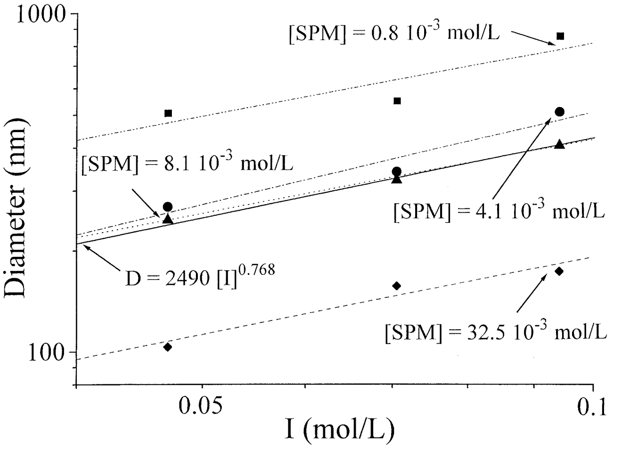


Fig. 5 Log–log variation of diameters with ionic strength at constant SPM concentration

concentration or the ionic strength in log–log graphs. The last stage of this analysis is to find an empirical equation like

$$\log D = A + B \times \log[\mathrm{SPM}] + C \times \log[I] \quad \text{or}$$
$$D = A' \times [\mathrm{SPM}]^B \times I^C . \tag{4}$$

Influence of SPM concentration at constant ionic strength. In Fig. 4, it is easy to see that particle diameters decrease with increasing SPM concentration, as it was found by Juang and Krieger [4] in emulsion polymerization of styrene in presence of NaSS.

The calculation of empirical relations gave the following equations (in each case the correlation coefficients were very good: >0.90):

$$I = 4.7 \times 10^{-2}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 27.54 \times [\mathrm{SPM}]^{-0.42} , \tag{5}$$

$$I = 7.05 \times 10^{-2}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 56.23 \times [\mathrm{SPM}]^{-0.33} , \tag{6}$$

$$I = 9.4 \times 10^{-2}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 45.71 \times [\mathrm{SPM}]^{-0.42} , \tag{7}$$

We also represented the average diameter $D_{\mathrm{nm}} = 41.02 \times [\mathrm{SPM}]^{-0.39}$ which was calculated with a very good correlation coefficient (0.90).

Influence of the ionic strength at constant [SPM]. In Fig. 5, the same results are represented as a function of ionic strength.

As for the influence of SPM, we found the same behaviour as Krieger and Ottewill: an increase of the ionic strength increases the diameter. The empirical equations, which were calculated with very good correlation coefficients except for $[\mathrm{SPM}] = 0.8 \times 10^{-3}$ mol/l (0.88), are presented below:

$$[\mathrm{SPM}] = 32.5 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 1088 \times [\mathrm{I}]^{0.757} , \tag{9}$$

$$[\mathrm{SPM}] = 8.1 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 2152 \times [\mathrm{I}]^{0.709} , \tag{10}$$

$$[\mathrm{SPM}] = 4.1 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 3973 \times [\mathrm{I}]^{0.894} , \tag{11}$$

$$[\mathrm{SPM}] = 0.8 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 4209 \times [\mathrm{I}]^{0.714} . \tag{12}$$

We also represented the average equation

$$D_{\mathrm{nm}} = 2490 \times [\mathrm{I}]^{0.768} \tag{13}$$

but the correlation coefficient was not as good as in the first case (only 0.38). This coefficient seems to indicate that the "log–log model" doesn't fit very well with the experimental results.

General equation. In the last stage of this analysis, we represented on one graph the variation of particle diameters with both the ionic strength and the SPM concentration. For that, we plotted the variation of diameters versus $[\mathrm{SPM}]^{-0.39} \times [\mathrm{I}]^{0.768}$ in Fig. 6.

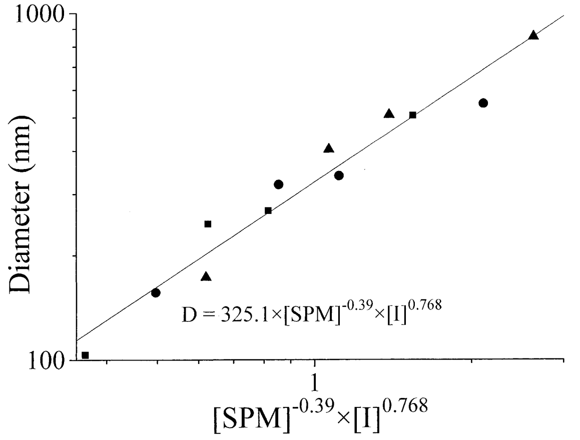


Fig. 6 Log–log variation of particle diameters versus $[SPM]^{-0.39} \times [I]^{0.768}$ with general experimental condition: (■) $I = 4.7 \times 10^{-2}$ mol/l, (●) $I = 7.05 \times 10^{-2}$ mol/l, (▲) $I = 9.4 \times 10^{-2}$ mol/l

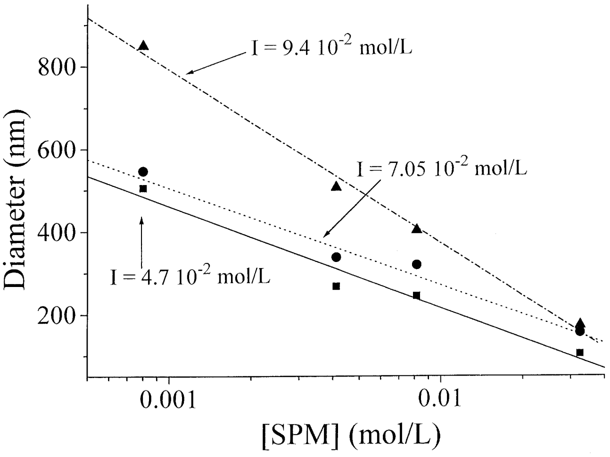


Fig. 7 Semi-log representation of particle diameters versus [SPM] at constant ionic strength

This general equation,

$$D_{\mathrm{nm}} = 325.1 \times [SPM]^{-0.39} \times [I]^{0.768} \quad (14)$$

was calculated with a very good correlation coefficient > 0.97. But in fact, this coefficient is not very representative since we saw in the former stage that the experimental results did not fit very well with the Eqs. (9)–(13).

If we compare Eq. (14) with Krieger's one [4] (Eq. (3)), we can see that the coefficients for the ionic strength are not very different: 0.64 found by Krieger and 0.77 by us. On the other hand, the coefficients for SPM concentration are quite different: −0.64 found by Krieger and −0.39 by us. This difference may be explained by the values of ionogenic comonomer concentration and ionic strength used by us and Krieger. We worked with larger ranges for the parameters, and we obtained larger variations for the particle diameters (see Table 2). Another explanation may be the difference in nature of NaSS and SPM.

Then we tried to find other fitting equations which could better explain our results.

Second analysis by semi-log or exponential equation

Influence of SPM concentration. On Fig. 7 the variations of diameters with SPM concentration were fitted by semi-log equations.

It has been possible to calculate three empirical relations for each ionic strength which show a semi-log variation of diameter with SPM concentration:

$$I = 4.7 \times 10^{-2}\ \mathrm{mol\,l^{-1}}, \quad D_{\mathrm{nm}} = -275.3 - 245.4 \times \log([SPM])\,, \quad (15)$$

$$I = 7.05 \times 10^{-2}\ \mathrm{mol\,l^{-1}}, \quad D_{\mathrm{nm}} = -197.0 - 237.0 \times \log([SPM])\,, \quad (16)$$

$$I = 9.4 \times 10^{-2}\ \mathrm{mol\,l^{-1}}, \quad D_{\mathrm{nm}} = -469.0 - 420.2 \times \log([SPM])\,, \quad (17)$$

where [SPM] is in mol/l.

It is interesting to note that for the two lower ionic strengths (15) and (16), the slopes are very close, whereas for the highest ionic strength (17), the slope is different. This phenomenon seems to indicate that the behaviour of the system is different for high and low ionic strengths.

Influence of ionic strength. Fig. 8 shows the variations of diameters with ionic strength.

In this case, we found three different behaviors according to SPM concentration.

For low SPM concentrations, 0.8×10^{-3} (18) and 4.1×10^{-3} mol/l (19), we found an exponential behavior of particle diameters versus I, as indicated in the following

Table 2 Comparison of our results with Krieger's ones

	[NASS] or [SPM] range [mol/l]	[I] range [mol/l]	Diameter range [nm]
Krieger [4]	3.64×10^{-3}–6.07×10^{-3}	2.94×10^{-2}–5.19×10^{-2}	181–346
Present work	0.8×10^{-3}–32.5×10^{-3}	4.7×10^{-2}–9.4×10^{-2}	103–850

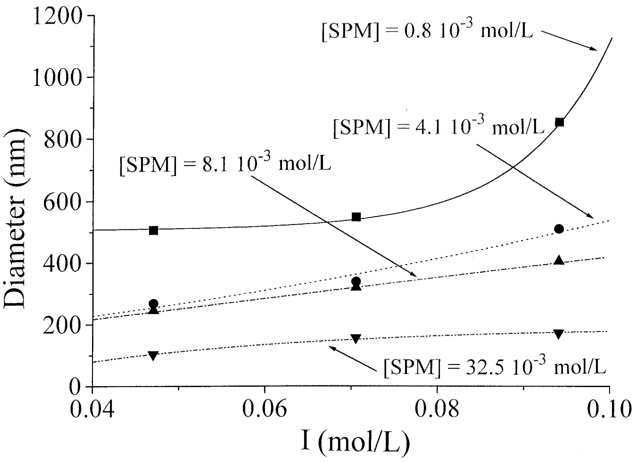


Fig. 8 Variation of particle diameters with ionic strength at constant SPM concentration

equations:

$$[\mathrm{SPM}] = 0.8 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 507.4 + 0.028 \times \exp(100 \times [\mathrm{I}]) , \quad (18)$$

$$[\mathrm{SPM}] = 4.1 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = -146.8 + 251.3 \times \exp(10 \times [\mathrm{I}]) . \quad (19)$$

For intermediate SPM concentration, 8.1×10^{-3} mol/l, the variation of diameter is directly linear versus I:

$$[\mathrm{SPM}] = 8.1 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 86.9 + 3344 \times [\mathrm{I}] . \quad (20)$$

For high SPM concentration, 32.5×10^{-3} mol/l, the variation of diameters is very weak and linear versus 1/[I]:

$$[\mathrm{SPM}] = 32.5 \times 10^{-3}\ \mathrm{mol/l}, \quad D_{\mathrm{nm}} = 145.8 - \frac{6.63}{[\mathrm{I}]} . \quad (21)$$

For each equation, the correlation coefficients are better than those we found with the log–log analysis (Eqs. (9)–(12)).

These different behaviours are probably due to SPM. If the concentration of SPM is too high (21), as well as acting as colloidal stabilizer, it also forms water-soluble homopolymers which probably modify the system. It is interesting to note that for these suspensions ([SPM] = 32.5×10^{-3} mol/l), washing by ion exchange resin was not possible. We had to use centrifugation to eliminate these homopolymers which are water-soluble.

We saw in the introduction of this paper that increasing ionic strength should increase particle diameters. Here, when SPM concentration is too high (21), the SPM effect (decreasing diameters) prevails over ionic strength effect (increasing diameters), resulting in a very low increase of diameters with I.

The SPM concentration of 8.1×10^{-3} mol/l (22) seems to be a transition value between an unusual behaviour due to a higher concentration and an expected one without SPM in excess.

Conclusion

In this paper, we synthesized latex particles of poly(styrene co-butylacrylate) with controlled size. The synthesis took place in the presence of ammonium persulfate as initiator and potassium sulfopropylmethacrylate (SPM) salt as ionogenic comonomer by emulsion polymerization.

The stabilization of particles is ensured both by sulfate functions from initiator and by sulfonate functions from SPM.

We studied the influence of two synthesis parameters on particle diameters, the SPM concentration, and the ionic strength, which is adjusted by variable quantities of sodium bicarbonate, $NaHCO_3$.

In these conditions, we were able to control particle diameters from 100 to 850 nm, with variations similar to literature values:

- increasing SPM concentration at constant ionic strength decreases particle diameters,
- increasing ionic strength at constant SPM concentration increases particle diameters.

We first analysed our results as Juang and Krieger by log–log equations. This analysis gave us quite good fittings. Then we suggested another analysis which indicated different behaviors of the system according to SPM concentration.

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