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High solids content emulsion polymerisation without intermediate seeds. Part I. Concentrated monomodal latices

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Abstract

In order to produce high solid content latexes in an unseeded process it is necessary to first begin by generating a concentrated latex with a monomodal particle size distribution and high solid contents. A process for the emulsion polymerisation of methyl methacrylate with butyl acrylate at solid contents of over 60% per unit volume is presented. The process relies on the use of an electrically neutral initiation system, combined with a stabilisation system rich in non-ionic surfactant. It was demonstrated that during the critical semi-batch growth stage, it is necessary to add the surfactant at a variable flow rate in order to avoid accumulating it in the water phase, and thereby ensuring that particles created by homogeneous nucleation are not stabilised. It is also shown that correctly adjusting the flow rate leads to a robust, reproducible process. Finally, a 'stability band' is clearly identified, and it is clear that the system is 'self-regulating' in the sense that an equilibrium between auto-flocculation and stabilisation of new particles leads to a latex with a surface coverage of 80–95% at high solid contents.

Keywords: High solid content; Latex; Viscosity

1. Introduction

In certain applications for which latices are used, e.g. pressure sensitive adhesives (PSA) or binders for paint, it is very useful to reach high polymer concentrations since increasing the polymer content can improve certain properties, e.g. reductions in the drying time, improved surface coverage, better films. It also helps to lower certain costs, especially by reducing transportation and storage costs. However, the viscosity of a latex increases sharply as the particles begin to enter into contact [1], and it is well-known that latex viscosity is strongly dependent on the polymer content, and the particle size distribution. Experimental evidence by a number of authors, including Schneider et al. [2] has shown that the relationship between the latex viscosity and the volume fraction is very similar to that shown schematically in Fig. 1.

At low solid contents (SC), the particles have relatively weak interactions, so the viscosity (η) remains low. As the SC increases, η increases slowly at first, then more and more rapidly as the SC approaches its maximum value (i.e. where the particles begin to interact very strongly, or even touch). At this point η increases extremely quickly. The behaviour in Fig. 1 is qualitatively the same regardless of the PSD of the latex, only the value of the limiting SC changes. The strategy behind producing high solid content/low viscosity (HSC/LV) latexes is therefore to develop a process to make a latex with a PSD that allows one to increase the limiting solid content.

Recent works have shown that latices composed of 85% (v/v) of large particles and 15% (v/v) of small particles offer satisfactory results when the ratio of the diameters of large to small particles is between 4 and 8 [2,3]. This same PSD is therefore chosen as a target in the current work. It should be mentioned that although no absolute proof exists to support the notion that this is the optimal PSD, significant amounts of experimental evidence show that latices with significant solids contents and low viscosities can be obtained with these values. As an indication of what 'high' viscosity is, in

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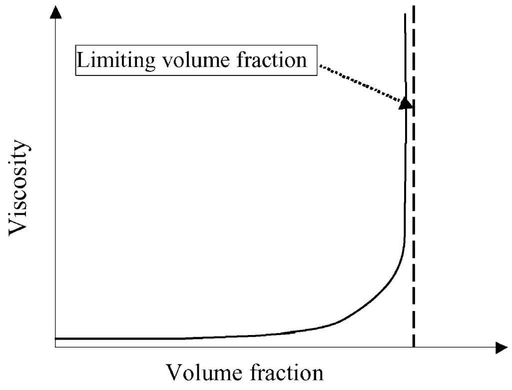

Fig. 1. Evolution of the latex viscosity as a function of the solids volume fraction.

their work on pressure sensitive adhesives, Schneider et al. [2,4,5] stated that for their applications, they wanted a viscosity below 1.5 Pa s at a shear rate of 20 s^{-1}. This definition will be adopted here.

Previously published results from our group have made it clear that this can be done using a bimodal PSD, but that a trimodal PSD offers very little in terms of solid content and viscosity, and furthermore trimodal PSDs can be hard to implement [4,5]. Obtaining such latexes poses a certain number of challenges, but simply put, the major challenge is to control the latex viscosity by manipulating the PSD during the entire process. A logical sequence of steps for the production of a bimodal PSD is shown in Fig. 2. One first produces an initial population of what will be the large particles in a semi-batch process. These particles are nucleated in Stage 1, and grown and concentrated in Stage 2. Care must be taken to avoid generating fines, as these will perturb the rheological properties. In addition, it is important to have created the correct number of particles at the end of Stage 2. Stage 3 involves the generation of a second population of small particles, and in Stage 4 both populations are concentrated to produce the desired latex.

The passage from Stage 2 to Stage 3 is the most delicate step, followed by Stage 4. It is a relatively straightforward exercise to produce the correct number of particles by the end of Stage 2. A number of patents (see review by Guyot et al. [3]), as well as work by Schneider et al. [5] and do Amaral Martins [6] have shown that different types of processes involving the blending and subsequent concentration of small and large seeds offer the possibility of reproducibly generating stable HSC/LV latexes—in other words, stage three is performed by injecting an intermediate seed of small particles into the reactor. However, these processes require the production, storage and additional manipulation of such seeds, and can therefore be onerous and costly from an industrial point of view.

Another possibility for the generation of the second population of small particles would be to create them directly in the reactor after producing an initial population of large particles. It has been shown [3–6] that renucleation of particles in situ via shots of initiator, monomer and/or surfactant can occasionally yield positive results. However, this type of process is often difficult to master, with highly irreproducible results and/or significant stability problems. Solids contents produced in this manner seem to be in the order of 65–68% (v/v) at best. Most of the difficulties associated with this type of process seem to stem from the destabilisation of the latex due to rapid particle generation. This generation of a large number of small particles is often worsened by the fact that a good number of the applications for which HSC latexes are used contain (partially) water-soluble monomers such as acrylic acid, itaconic acid, methyl methacrylate, and others. This type of product obviously favours the generation of particle via homogeneous nucleation throughout the reaction. In addition, the use of persulphates, or other compounds that generate electrically charged radicals favour the creation of such

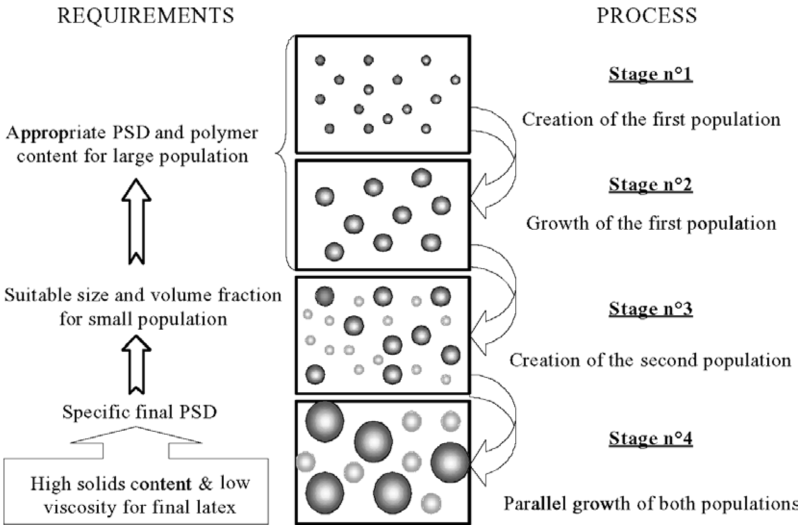

Fig. 2. Scheme of the general process for the synthesis of a HSC/LV latex.

small particles. In the event that a large number of small particles (with respect to the amount of surfactant available) are created rapidly, this can provoke a rapid and disastrous redistribution of the surfactant already present on the surface of the existing particles. If this happens, the latex can coagulate (totally or partially). And even if one only experiences a partial loss of stability, it can be very difficult to control the PSD with the precision necessary to maintain good rheological properties at moderate to high solid contents. This, and other similar problems are at the origin of a poor control over the PSD.

The objective of this paper and Part II [7] is to detail a means for the production of a high solid content latex with low viscosity, using a recipe similar to that used in the previously published papers from this research group [4,5, 8]. The polymer in question is composed of 78–80% (w/w) of butyl acrylate (BA), 20% (w/w) of methylmethacrylate (MMA), and 0–2% methacrylic acid (MAA). This was chosen as being a model composition for pressure sensitive adhesives. The latex will be stabilised by a similar combination of anionic and non-ionic surfactants. Schneider et al. [4,8] used a process based on in situ nucleation to create bi- and trimodal latexes, and were able to reach 68% (v/v) solids. In the follow-up paper [5], they used a seeded process to reach 73% solids. While the reproducibility of these processes and the rheological characteristics of the resulting latexes were satisfactory, the authors needed to create seeds of different sizes and to use both oil and water soluble initiators to reach this goal. In the current series of papers, a new means of reaching well over 70% solids with very low viscosity without the use of intermediate seeds or oil soluble initiators will be presented—otherwise stated, it is desired to perform all of the steps in Fig. 2 in one reactor without intermediate seeds. In addition, one of the key criteria for success here will be the reproducibility of the process.

This papers deals with the synthesis of the first population, and its concentration to approximately 60% polymer per unit volume (v/v) (i.e. steps 1 and 2 of Fig. 2). A number of points must be taken into consideration when defining the desired PSD for this population of particles. First of all the reaction time after the nucleation of the second population cannot be too long since it is difficult to maintain the ratio of the particle diameters within the correct range. This means that we have to reach the highest polymer content as possible with the first population of particles. As discussed by Schneider et al. [4], in order to reach a solid content of about 60% volume we need particle diameter of at least 500–550 nm (if the diameter is much lower than this, the viscosity at 60% v/v solids will be too high and it will be necessary to dilute the latex to continue with the second population). Secondly, depending upon how the second population of particles is created, they will tend to be on the order of 150–250 nm in diameter at the end of the nucleation phase [9,10]. Therefore, in order to obtain the correct PSD, and to maintain the ratio of volume fractions and sizes of the different populations, diameter ratios a priori required, we do not need a diameter much greater than 600–650 nm for the first population. Hence, the target for the first population will be monomodal latex with a polymer content of about 60 wt%, and a particle diameter at least equal to 500 nm which corresponds to a number of particles $N_p \leq 1 \times 10^{16}$ particles per litre.

2. Experimental

The monomers used in this study were methylmethacrylate (MMA), butyl acrylate (BA) and methacrylic acid (MAA). The copolymers always contained 20% by weight MMA, and 78–80% by weight BA, with the difference being made up from MAA. The initiators used in the experiments were ammonium persulphate (APS), or the redox pair hydrogen peroxide/ascorbic acid (HPO/AscA). All products were obtained from ACROS (Isle d'Abeau, France) and used as received. The anionic surfactant (TA) was Disponil® FES 32 IS (sodium salt of ethoxylated fatty acid with sulphate groups), and the non-ionic surfactant (TN) was Disponil® A 3065 (mixture of linear ethoxylated fatty acids with alcohol end groups). Both surfactants were supplied by Cognis (France) and used as received, and were characterised by Schneider et al. [8].

All reactions were carried out in 1 or 3 l, jacketed glass reactor connected to heated water bath for temperature control. Samples were occasionally withdrawn through a valve in the bottom of the reactor for analysis. In order to facilitate the discussion, the different recipes used will be detailed during the discussion of the results.

Conversions were measured by gravimetry. Average particle sizes were measured by Quasi-elastic light scattering (QELS) with a Malvern Lo-C, or by static light scattering using a Beckman-Coulter LS-230 (also used for full PSD). Average particle sizes from the Lo-C reported here are averages of 10 measurements per sample, whereas the full PSD provided by the LS-230 is an average taken over three measurements of the same sample. Viscosity was measured using a Rheometric Scientific Viscometer (RFS III) at room temperature.

3. Results and discussion

Different strategies were explored in order to synthesise the first population with these points in mind. Simply speaking, the population is created by batch polymerisation at a solid content of 10 or 20% (w/w). A semi-batch stage is then carried out in order to concentrate the latex and cause the particles to grow. We focused most of our attention on the semi-batch period in this chapter, as it has the most influence on the control of the PSD. The study has been divided into two parts. First, we expose the results of the different procedures tested for reactions initiated by APS.

Then we will focus on the use of the redox system as initiator.

3.1. Initiation by APS

As was just mentioned, one of the main difficulties is to avoid massive renucleation. Given that 20% (w/w) of the monomer is MMA, homogeneous nucleation will occur throughout the semi-batch growth period [11]. Thus, to minimise the stabilisation of particles created in this manner, it would be common practice to carry out the reaction under starved conditions, and avoid an excess of surfactant in the reactor (i.e. avoid creating too many particles).

In an initial attempt to reduce the amount of surfactant needed to create the large particles, surfactant-free batch polymerisations were carried out since it is well-known that when APS (or any other initiator yielding electrically charged radicals) is used as the initiator, it is possible to make a latex with no surfactant. Boutti et al. [9,12] showed that this is not possible with the HPO/AscA system because of the lack of charges. In this sense, APS is useful since it can be used to minimise the amount of surfactant in the medium during the batch stage. The nature of the emulsifier and the operating procedure for the semi-batch growth period were modified in two ways. For the first series of experiments, non-ionic emulsifier was added during the semi-batch step, and for the second one, anionic surfactant was used during the semi-batch. There is no real reason to use mixed surfactant systems here since the CMC of a mixture is lower than that of each emulsifier alone, and thus using a mixture of TA and TN would favour the nucleation of new particles.

The nomenclature of the runs respects the following rule: E2 corresponds to experiments concerning the second stage of the process (growth of the first population). Then, the second number (E2.1) designates the number of the series of experiments. Finally the third number indicates the number of the run. So, E2.11 is the first run of the series of experiments using APS and where TN is added during the semi-batch for the growth of the first population. E2.2x concerns the series of experiments using APS and where TA is added during the semi-batch, and E2.3x concerns the series of experiments using the redox couple HPO/AscA as initiator and where TN is added during the semi-batch. The polymerisation temperature was fixed at 70 °C. In the batch portions of the experiments, the reactants were purged with nitrogen, the emulsion was homogenised by stirring as temperature was increased to 70 °C, and the reaction was assumed to begin with the addition of APS (0.1 wt% with respect to the total volume of emulsion in all runs). The theoretical polymer content for the batch period is 10 wt% except for run E2.17 where it was 15 wt%. The semi-batch begins after 2 or 3 h of reaction time. For the semi-batch stage the procedure changed according to the run. The different procedures tested for each run are summarised in Table 1, and the detailed recipes are given in Table 2.

The differences between the runs are as follows:

- E2.11 and E2.12: the differences between these two experiments are the monomer and initiator flow rates.
- E2.13 and E2.14: the addition of surfactant at the end of the batch period allowed us to cover the particles before the beginning of the semi-batch stage.
- E2.15: the reactants were added separately, and the stabiliser solution was added according to a time-varying addition profile. This addition profile is calculated in such a way that the amount of surfactant added per hour just covers the newly generated surface area (assuming N_p constant).
- E2.16 and E2.17: E2.16 is a seeded semi-batch and the seed latex is E2.15. However, for these runs the experimental procedure is the same as for run E2.15 except the supplementary addition of a buffer solution.

3.1.1. Addition of non-ionic surfactant during the growth phase

Note that in the context of this work, it is important to keep in mind that the surface coverage corresponds to the fraction of the particle surface covered by surfactant molecules assuming no partitioning (i.e. all surfactant added is said to be adsorbed on the particles). We do not take into account the particle surface covered by charges coming from the persulphate initiator. A surface coverage greater than 100% means that there will be an excess surfactant in the water phase.

E2.11 and E2.12. For the two first runs a pre-emulsion is added at the end of the batch. The composition of the pre-emulsion is calculated as a function of the PSD at the end of the batch and the final characteristics desired for the final latex ($d_p > 500$ nm and $N_p < 10^{16}$ per litre). The flow rate of the pre-emulsion is calculated in order to obtain a monomer flow rate that maintains the system under starved conditions. The composition and flow rate of the pre-emulsion were chosen in order to ensure that the surface coverage remains below 100%. The recipe for E2.12 was modulated as a function of the results obtained for the run E2.11. Given that coagulum was formed during E2.11, the fraction of surfactant with respect to the amount of monomer was increased during run E2.12 in order to improve the stabilisation.

The evolution of the PSD as a function of the reaction time is shown in Fig. 3 and the main characteristics of the latex at the end of each stage for these experiments are given in Table 3.

First of all we note that at the end of each stage, the polydispersity index provided by the Malvern Lo-C (I_p) is relatively high (according to the manufacturer, a latex is monodisperse if I_p is less than 0.1, otherwise it is considered polydisperse and we can no longer have confidence in the

Table 1
Procedures tested for semi-batch stage

Run	Experimental procedure
E2.11	Addition of a pre-emulsion
E2.12	Addition of a pre-emulsion
E2.13	Particle coverage at the end of the batch + addition of a pre-emulsion
E2.14	Particle coverage at the end of the batch + addition of a pre-emulsion
E2.15	Addition of neat monomer and solution of APS at a constant flow rate + addition of the surfactant according to an addition profile
E2.16	Addition of neat monomer and solution of APS at a constant flow rate + addition of the surfactant according to an addition profile + addition of a buffer solution
E2.17	Addition of neat monomer and solution of APS at a constant flow rate + addition of the surfactant according to an addition profile + addition of a buffer solution

Table 2
Semi-batch procedures initiated by APS and with addition of TN. All the recipes and flow rates are indicated for 100 g of polymer in the batch charge. Surfactant quantities are given in terms of active matter

	E2.11	E2.12	E2.13	E2.14	E2.15	E2.16	E2.17
Batch stage[a]							
Water	900	900	900	900	900	–	850
BA	80	80	80	80	80	–	80
MMA	20	20	20	20	20	–	20
TN	0	0	0	0	0	–	0
TA	0	0	0	0	0	–	0
APS	1	1	1	1	1	–	1
Duration	120	102	120	125	185	–	180
Semi-batch stage							
Surfactant injection at the end of the batch[a]							
Water	–	–	76.6	75.3	–	–	–
TN	–	–	3.22	3.17	–	–	–
Pre-emulsion							
Water[a]	328	337	335.5	330.5	–	–	–
Monomer[a]	1165	1145	1140	1120	–	–	–
TN[a]	9.24	18.5	6.44	6.82	–	–	–
APS[a]	1.6	1.6	1.8	1.5	–	–	–
Feed flow	353	252	446	439	–	–	–
Feed duration	240	370	120	170	–	–	–
Neat monomer							
Feed flow	–	–	–	–	88	20	58
Feed duration	–	–	–	–	290	300	360
Aqueous solution							
Water[a]	–	–	–	–	12.4	20	75.9
APS[a]	–	–	–	–	0.9	–	0.84
$NaHCO_3$[a]	–	–	–	–	–	0.68	6.43
Feed flow	–	–	–	–	Shot	6.7	8.4
Feed duration	–	–	–	–		130	240
Non-ionic surfactant solution							
TN[a]	–	–	–	–	7.7	1.7	12.6
Water[a]	–	–	–	–	147.5	34.2	184.4
Feed flow							
1st hour	–	–	–	–	32	5.3	15.8
2nd hour	–	–	–	–	29.1	5.1	14.5
3rd hour	–	–	–	–	26.6	4.9	13.2
4th hour	–	–	–	–	25.1	4.7	12.6
5th hour	–	–	–	–	–	4.4	11.9
6th hour	–	–	–	–	–	–	11.3
Finishing period[b]	40	24	–	5	35	60	–

Feed flows in g/h.

[a] All the amounts are indicated in grams.

[b] Duration in minutes.

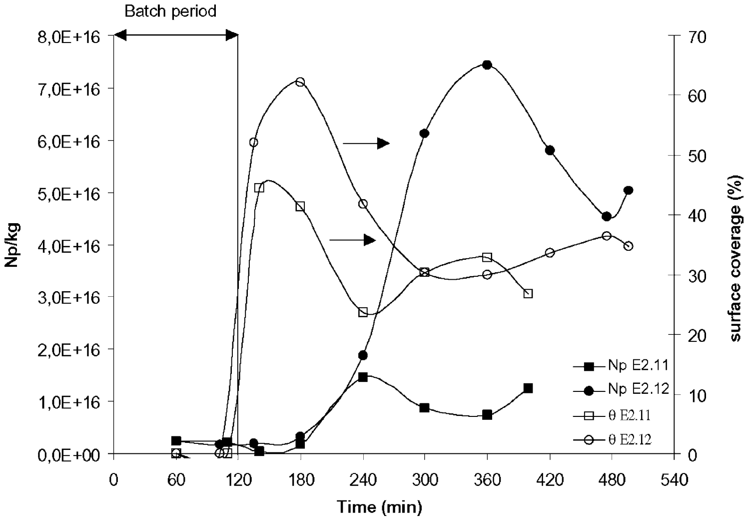

Fig. 3. Evolution of the PSD versus reaction time for runs E2.11 and E2.12.

absolute value of the diameter measured at a fixed angle of 90°). This signifies that the PSD obtained are wide. The PSD in such cases depends on the particle surface charge density [13,14]. However, the charge density scales with different parameters such as the particle diameter, but also the average molecular mass of the polymer or different factors such as the type of termination reaction (combination or disproportionation) or the fact that uncharged radicals can start chain growth even in the case of ionic initiators [14]. So, the surface charge density upon which the PSD depends, is a function of a certain number of parameters that are not necessarily reproducible.

This lack of reproducibility might be due to the fact that a part of the charges provided by the initiator is buried during the polymerisation and this does not necessarily occur in the same way for all of the runs. In addition, if the PSD is more or less complex (i.e. broad, or multimodal) the technique used for particle size measurements (PCS at 90°) is not well adapted [15,16], so the results have to be considered with caution. However, at the time these experiments were performed, PCS at 90° (Malvern Lo-C) was the only method available for the measurement the PSD, and the results in Fig. 3 are therefore calculated in this way.

The high value of I_p at the end of the semi-batch stage is less surprising. Indeed, as can be seen in Table 3, coagulum was formed in both experiments, but the system was not entirely destabilised. As can be seen in Fig. 3, significant renucleation occurred during both reactions, and the higher amount of surfactant present in E2.12 did not reduce the amount of coagulum. Indeed, the additional surfactant seems to favour the renucleation even more in E2.12. For the first hour of the semi-batch stage, N_p and θ remained more or less stable. Then some time between 180 and 240 min, a significant number of particles are generated in both experiments. The high surface area developed by these small particles probably caused a redistribution of the surfactant, which was initially adsorbed onto the particles. This in turn could have partially destabilised the system and led to the formation of coagulum. Interestingly enough, the particle generation in these two experiments took place in such a way that the final surface coverage of surfactant was approximately the same. These results show that the concentration of stabiliser is a delicate parameter to adjust [17]. Given that a higher amount of surfactant added during the semi-batch stage seems to favour the renucleation, an attempt was made to increase the stability by covering the particles at the end of the batch, rather than during the initial part of the semi-batch phase.

E2.13 and E2.14. For these runs we chose to cover the particles at the end of the batch in order to increase the stability before the addition of the pre-emulsion. The main characteristics of the latex at the end of each stage are given in Table 4.

It can be seen that E3.13 has a broad PSD, whereas there is a monodisperse population at the end of the batch E3.14. These results confirm that the surfactant-free batch period is not particularly reproducible.

The procedure tested for runs E2.13 and E2.14 led to the

Table 3
Main characteristics of the latex for runs E2.11 and E2.12

Run	End of the batch period					End of the semi-batch period					
	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	Final stability
E2.11	9	428	0.3	0.21	0	49	411	0.2	1.2	27	Coagulum (2%)
E2.12	9	448	0.6	0.17	0	48	256	0.2	4.9	35	Coagulum (4.7%)

Table 4
Main characteristics of the latex at the end of the batch and at the end of the semi-batch stages for runs E2.13 and E2.14

Run	End of the batch period					End of the semi-batch period					
	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	Final stability
E2.13	9	371	0.3	0.31	130	30	198	0.4	6.9	23	Coagulum (22%)
E2.14	9	342	0.04	0.39	117	41	176	0.2	13	16	Coagulum (16%)

formation of a significant amount of coagulum, and even higher amounts of renucleation than in the previous runs. Actually, the surface coverage (calculated by simply assuming that all surfactant is absorbed on the surface of the latex. This is obviously false, but provides a reasonable upper limit) at the beginning of the semi-batch is very poorly adapted, and is apparently much too high, which favoured the formation of new particles. As mentioned above, the high surface area developed by small particles involves a redistribution of the surfactant, which destabilises the system. A lower surface coverage at the end of the batch might improve the results.

E2.15, E2.16 and E2.17. In these three runs, the reactants were added separately in order to allow a better control of the surfactant concentration in the medium. Since the first series of experiments gave slightly better results than the second, it was decided not to provide additional surface coverage at the end of the batch. Instead TN is added according to an addition profile. The addition profile is calculated in such a way that we add just enough surfactant

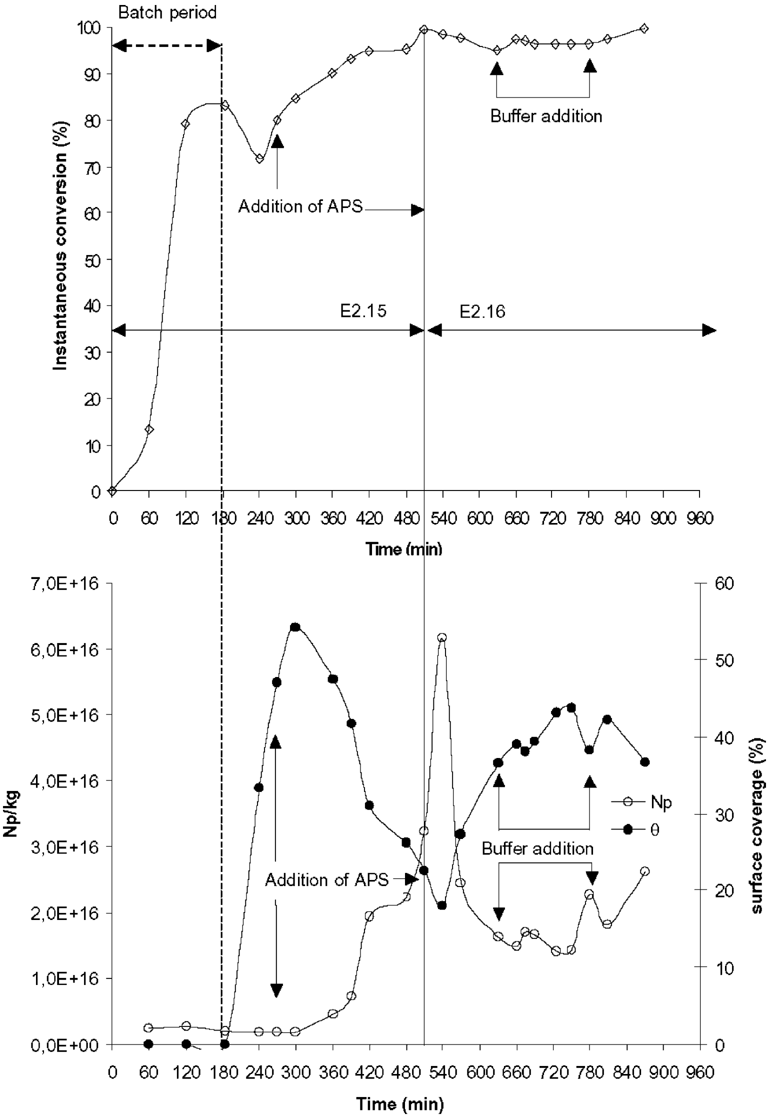

Fig. 4. Evolution of the instantaneous conversion and the PSD as a function of the reaction time for runs E2.15 and E2.16.

Table 5
Main characteristics of the latex at the end of the batch and at the end of the semi-batch stages for runs E2.15, E2.16 and E2.17

Run	End of the batch period					End of the semi-batch period					
	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	Final stability
E2.15	8	417	0.4	0.2	0	35	268	0.3	3.1	22.5	Stable
E2.16	–	–	–	–	–	47	318	0.2	2.6	37	Coagulum (5%)
E2.17	14	500	0.08	0.2	0	39	275	0.4	3.2	29	stable

to cover only the newly generated surface area (assuming that N_p remains constant!) and that all of the surfactant added is adsorbed on the particles. In E2.16 and E2.17 the impact of the addition of a buffer solution on the number of particles was also studied (c.f. Table 2). Neat monomer is added at a constant flow rate during the run E2.15, and two shots of APS are added during the semi-batch stage at 270 and 520 min as indicated in Fig. 4. E2.16 is a seeded semi-batch polymerisation, and the seed latex is E2.15. Before the beginning of the semi-batch, the seed is swollen with 5 wt% of monomer (with respect to the amount of polymer) and an additional amount of APS is added. Then, neat monomer is added at a constant flow rate, non-ionic surfactant is added according to the addition profile shown in Table 2, and a buffer solution is added during 2 h as indicated in Fig. 4.

For E2.17, during the semi-batch stage, non-ionic emulsifier is added according to the profile shown in Table 2, neat monomer and an aqueous solution of buffer and APS were added at constant flow rates of 58 and 8.4 g/h, respectively, for 4 h. The main characteristics of the latex at the end of each stage are presented in Table 5

The evolution of the instantaneous conversion and the particle size as a function of time for runs E2.15 and E2.16 are presented in Fig. 4. During the semi-batch step of E2.15 a significant increase of N_p can be seen after the addition of APS. This renucleation is followed by a flocculation stage, which leads to the formation of coagulum (5%). The evolution of the PSD is shown in Fig. 5 for run E2.17. For this experiment the initiator has been added to the buffer solution. A significant increase in N_p was once again observed as soon as the addition of this aqueous solution began.

It clearly appears that the addition of APS provokes a significant renucleation of particles (or more accurately a stabilisation of homogeneously nucleated particles) even though there are no micelles, or even an excess of TN. The calculations show that the surface covered by TN is at most 55% for the last three experiments, and 65% for E2.12. Note also that it has been assumed that the surfactant does not partition between the water and particle surface. In addition, given the high polydispersity of these latices, the real surface area is likely to be higher than that estimated using an average value of d_p. Both of these reasons indicate that the value of θ calculated here is an overestimate of the real fractional surface coverage. Indeed, as was suggested previously, one of the main parameters that control the stabilisation is the surface charge density, and in these experiments the charges are provided by APS. Thus, despite the low surface coverage provided by TN, homogeneously renucleated particles are stabilised by SO_4^- end-groups, as in the case of surfactant-free polymerisations. Also, the addition of the buffer solution seems to have no influence on the number of particles in either experiment, not even during the semi-batch of E2.16 where it is added without APS. This might be due to the fact that charges provided by APS are sufficient for the renucleation, but once small

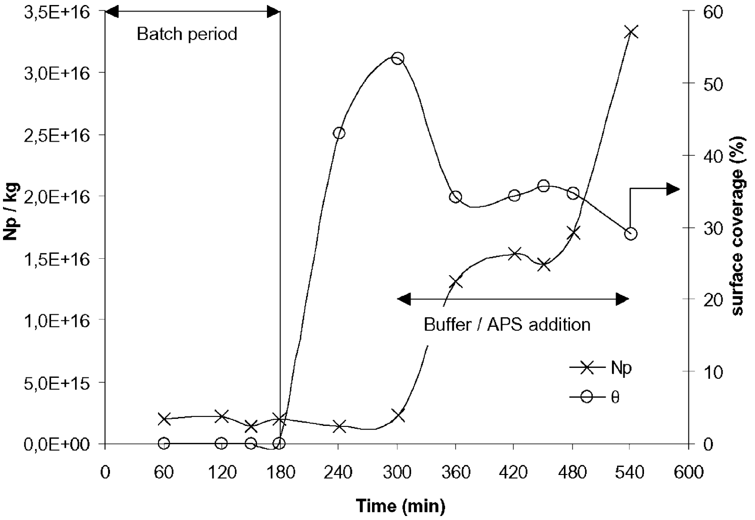

Fig. 5. Evolution of the number of particles and the surface coverage as a function of the reaction time for the run E2.17.

Table 6
Composition and flow rate of the pre-emulsion for runs E2.21 and E2.22

Pre-emulsion composition (g)	E2.21	E2.22
Water	335.44	340.20
TN	0.00	0.00
TA	2.91	2.45
Active matter	0.93	0.78
Water	1.98	1.67
APS	1.53	1.56
MMA	223.30	227.94
BA	896.12	901.47
Pre-emulsion flow rate	5.2 g/min	2.9 g/min

particles are nucleated the stabilisation of the system is also assured by TN. Since steric stabilisation is quasi-insensitive to the ionic strength, the buffer has no influence on N_p.

Given that the presence of charges seems to control the stabilisation of homogeneously nucleated particles, it might be easier to control the PSD using an anionic surfactant. In order to better understand the phenomena involved, we carried out a pair of experiments with addition of anionic surfactant during the semi-batch stage.

3.1.2. Addition of anionic surfactant during the growth

The concentration of anionic surfactant in the pre-emulsion was calculated in order to reach a very low final surface coverage of about 15% (assuming that N_p is constant after the batch phase). The flow rate was adjusted in order to be in starved conditions. Table 6 gives the composition and the flow rate for the pre-emulsion for both experiments. The difference between these two experiments is the flow rate of the pre-emulsion. The main characteristics of the latex at the end of each stage are summarised in Table 7.

It can be observed here that the number of particles at the end of the batch stage is higher for run E2.21 than in the previous runs. This is due to an inhibition period that occurred at the beginning of this stage. Thus, when the semi-batch stage began the conversion was only about 75% and the particles were smaller and more numerous since the limited flocculation was not completed. However, insofar as the polydispersity index at the end of the batch step is concerned, the same variability was noted in these two runs as was seen above. Indeed, for both of these runs, the Malvern Lo-C indicates a narrow PSD.

The evolution of the number of particles, the surface coverage and the polydispersity index as a function of the reaction time for runs E2.21 and E2.22 are presented in Fig. 6. These experiments reveal a number of interesting points. First, it can be seen that the final surface coverage is twice as low as the value expected, but is nevertheless sufficient to assure the stability of the latex. Moreover, the same final value is found for both experiments, despite the different particle sizes obtained. A significant increase in N_p occurs between 360 and 420 min during run E2.22. Why this renucleation occurs here is not entirely clear. The surface coverage appears to be very similar in both experiments; however it is not possible to calculate the exact value since the polydispersity index is high throughout the semi-batch stage. Regardless of its origin, the renucleation is followed by a limited flocculation, which pushes the system toward a surface coverage of approximately 8%. Unfortunately, at this stage of the study, we did not have access to a particle size analyser capable of giving us a full PSD. However, had we had one, it is entirely possible that these latices would have had bimodal PSD given the I_p of the final products.

In order to try to better understand these results, we attempted to interpret them in terms of the surface charge density. In order to do so, the density of electric charges on the surface of a surfactant-free latex was measured to estimate the minimum density required to stabilise the particles. The latex analysed was a surfactant-free product with a polymer content of 10% (Boutti et al. [12]). After the surfactant-free polymerisation, the latex was diluted and cleaned by passing it over ion exchange resins until a constant value of conductivity was reached. The surface charge density was measured by titrating the latex with NaOH to determine the number of sulphate groups (SO_4^-). This analysis revealed that the colloidal stability was ensured by a charge density of about 7 $\mu C/cm^2$ at the particle surface. Given the concentration of APS used for this polymerisation, this means that approximately 25% of the charges provided by APS are on the particle surface. Assuming that a similar fraction of the initiator is buried during the runs presented here, the evolution of the surface charge density was calculated for runs E2.21 and E2.22. This is shown in Fig. 7, along with the number of particles.

It can be seen that the evolution of the number of particles and the evolution of the density of charges on the latex surface are closely correlated. An increase of the number of particles corresponds to a decrease of the charge density. These results suggest that the surface area (or equivalently the number of particles) evolves in such a manner that the system arrives at a limiting surface charge density (since we are dealing exclusively with electrosteric stabilisers here), which is adequate for the stabilisation. Indeed, the system seems to oscillate in order to reach a charge density of between 4.5 and 5 $\mu C/cm^2$ (according to

Table 7
Main characteristics of the latex at the end of the batch and at the end of the semi-batch stages for runs E2.21 and E2.22

Run	End of the batch period					End of the semi-batch period					
	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	PC (%)	d_p (nm)	I_p	N_p/kg $\times 10^{16}$	θ_F (%)	Final stability
E2.21	8	275	0.06	0.66	0	51	670	0.4	0.3	8	Stable
E2.22	9	365	0.1	0.27	0	50	763	0.8	0.2	8	Stable

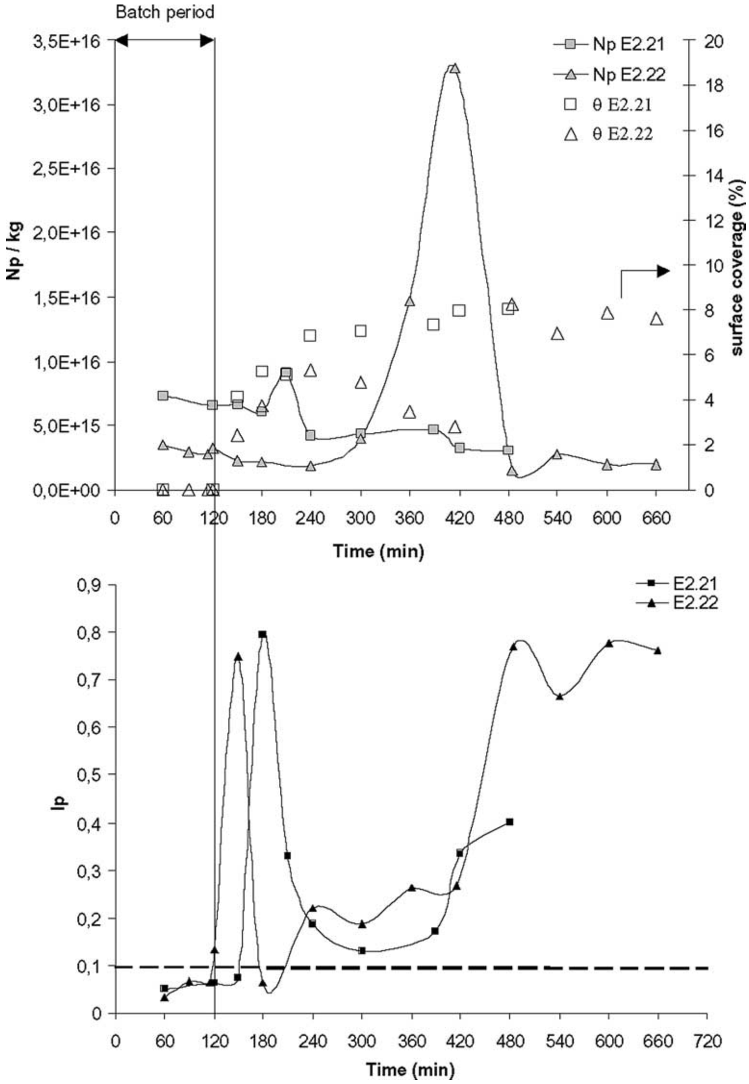

Fig. 6. Evolution of N_p and θ as well as the polydispersity index versus reaction time for runs E2.21 and E2.22.

the hypotheses used here). Despite the approximations used in the calculation of the charge density, this value is close to the one measured for the surfactant-free latex. The slight difference observed between the two values can be explained by two phenomena. First of all, it is possible that the fraction of charges from the initiator that are situated on the particle surface is higher than 25% for a semi-batch experiment, this would mean that the charge density calculated in the manner described above is slightly underestimated. However, more importantly, a part of the stabilisation in runs E2.21 and 2.22 is due to the anionic surfactant. Given that this surfactant contains approximately four ethylene oxide groups per molecule, the stabilisation is, strictly speaking, electrosteric (although Fortuny et al. [11, 18] showed that this product behaves like an electrostatic stabiliser). These experiments allowed us to show once again that the evolution of the PSD is defined, in large part, by the surface charge density. However, the PSD is not well controlled during these polymerisations, and the final PSD obtained in this manner are very broad ($I_p = 0.4$ and 0.8). Also, the final surface coverage of the surfactant is very low ($\theta \approx 8\%$), which could become a significant drawback when trying to reach high polymer contents and at the same time attempting to control the level of stabilisation in order to induce a controlled renucleation. This, combined with the presence of a certain number of fine particles which are detrimental to the rheological properties at high solids content, means that it is preferable to create the population of large particles in a different way.

Given the experimental conditions (i.e. the presence of MMA), homogenous renucleation always occurs, but the stabilisation of these small particles depends on the composition of the medium. In the experiments where the reactants were added separately, it was observed that the addition of initiator was followed by massive renucleation. So, for systems stabilised by non-ionic surfactant the charges provided by APS are more than sufficient to allow the stabilisation of the renucleated

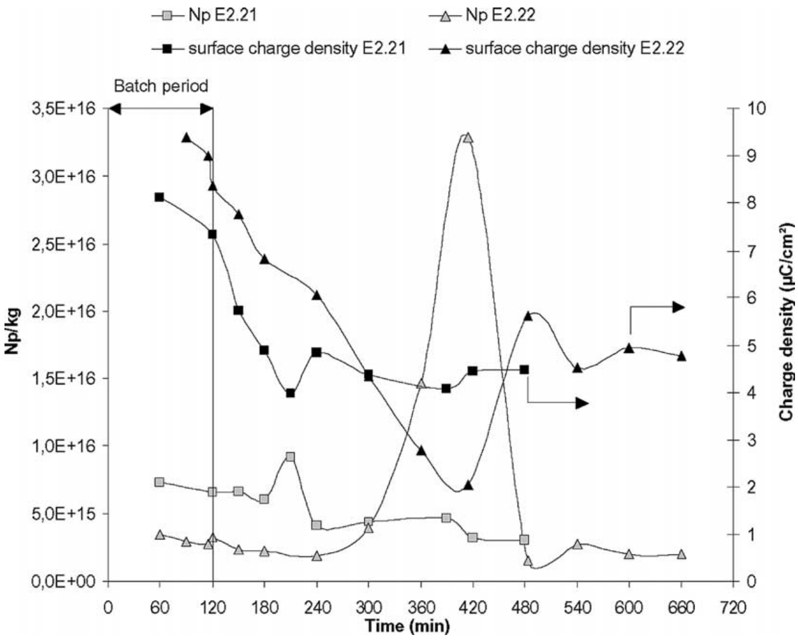

Fig. 7. Evolution of N_p and the surface charge density for runs E2.21 and E2.22.

particles, despite the low TN concentrations used ($\theta <$ 30%).

In the experiments with TA alone, the surface coverage provided by the anionic surfactant was much lower (8% at most) than that obtained with TN, and the latices were macroscopically stable. Moreover, during the semi-batch stage the PSD seemed to oscillate between renucleation and flocculation to reach the same final surface coverage regardless of the particle size. According to the rough calculations done here, it appears that the system is 'auto-regulated', i.e. the particles are driven to 'reorganise' themselves in order to reach a certain density of charges.

Finally it seems difficult to avoid the stabilisation of renucleated particles for systems initiated by APS. Indeed, the stabilisation due to the charges provided by the initiator makes the control of the global stability especially delicate. As mentioned earlier, the I_p of these latices are so high that they cannot be considered monodisperse (in fact, the indices are high enough that experience suggests that the PSD might even be bimodal at this point—however, even were this the case, the particles would not be of a sufficiently different size to allow us to concentrate them to high solid contents at low viscosities).

In order to overcome these difficulties we chose to modify the nature of the initiator and use the redox system H_2O_2/AscA, which does not generate charged radicals, and thus has no influence on particle stabilisation (other than generating oligoradicals of course).

3.2. Initiation by the redox system H_2O_2/Ascorbic acid

Since it is not possible to create particles in absence of charges (i.e. we cannot use HPO/AscA with TN alone) it is necessary to use a mixed surfactant system to create the particles in the initial batch stage (Boutti et al. [12]). However, as shown in the preceding section, the objective here is to minimise the amount of charges present in the medium in order to better control the stability, and thus the PSD. Furthermore, the preceeding results also suggest that one way of obtaining the PSD specified in the introduction is to impose conditions during the semi-batch step in order to prevent the stabilisation of the homogeneously nucleated particles. This kind of procedure can lead to limited flocculation of the continually appearing particles, and thus can lead to a decrease of N_p. Given that we want to create a PSD with $N_p \leq 1 \times 10^{16}$ particles per litre, experience showed that we need to create approximately twice this number of particles during the batch period if we allow limited flocculation to occur during the subsequent step. In order to reach a solid content on the order of 55–60% as quickly as possible, the polymer content for the batch was fixed at 20 wt%.

Under these conditions, it was found that the correct choice of a mixture of TA and TN allowed us to make approximately 2.5×10^{16} particles per litre with a diameter of about 250 nm. The surfactant system concentration is about 3.6 g/kg, and the anionic stabiliser represents 0.5 wt% of the total amount of emulsifier ($\sim$0.02 g/kg) (Schneider [19]).

At the end of the batch period we have a polymer content of 20% per unit volume and approximately 2.5×10^{16} particles/kg with a diameter of 250 nm. The surface coverage (θ) is much lower than 100% (generally closer to 50%) and the latex is stable. This state of colloidal stability (d_p, N_p, θ) is an equilibrium determined by the system. It should be pointed out that the surface coverage is

Table 8
Main characteristics of the latex at the end of each stage

Run	End of the batch period						End of the semi-batch period					
	PC (%)	d_p (nm)	I_p	N_p/kg × 10^{16}	θ_F (%)	$\theta_{applied}$ (%)	PC (%)	d_p	I_p	N_p/kg × 10^{16}	θ_F (%)	$\theta > 100\%$
E2.34	18	250	0.06	2.0	46	100	44	490	0.09	0.66	89	No
E2.36	18	256	0.10	1.9	47	100	44	444	0.10	0.89	87	No
E2.38	18	292	0.09	1.3	51	100	46	560	0.10	0.46	91	No
E2.39	18	265	0.07	1.7	46	100	48	560	0.09	0.48	81	No
E2.310 Q_{TN}: cst	19	253	0.06	2.1	56	100	61	617	0.09	0.46	78	No
E2.313	17	250	0.04	2.1	50	80	62	570	0.12	0.59	75	No
E2.314	19	272	0.06	1.6	52	90	58	569	0.09	0.56	84	No
E2.315	19	216	0.08	3.3	41	90	63	547	0.09	0.68	87	No
E2.319	17	258	0.04	1.7	56	85	49	478	0.04	0.79	90	No
E2.320	16	267	0.06	1.0	54	85	59	553	0.10	0.62	78	No
E2.321	15	286	0.08	1.1	70	85	61	534	0.15	0.71	83	No
E2.323	16	279	0.05	1.3	63	100	63.5	423	0.21	1.5	77	Yes
E2.327	18	260	0.08	1.8	47	90	59	507	0.12	0.80	81	No
E2.328	18	230	0.07	2.6	43	90	59	580	0.12	0.54	91	No
E2.329	17	222	0.04	2.8	43	90	59	618	0.11	0.44	97	No
E2.330	19	276	0.07	1.6	48	100	60	540	0.12	0.69	78	No

All values of d_p shown here are obtained by PCS at a fixed angle of 90°.

calculated assuming that the total amount of surfactant is located on the particle surface. However, it has been shown that it is not always the case [20]. Nevertheless, given the stabilisation system used in this section, even if the surfactant is partitioned at $\theta < 100\%$ it is unlikely that large quantities of surfactant, and especially TA, are present in the water phase.

To control the PSD it is necessary to avoid accumulating free surfactant molecules during the semi-batch stage, and above all to avoid the formation of micelles. This means that it is judicious to add just enough TN during the semi-batch phase to cover the new surface generated by particle growth. This addition profile was calculated by assuming that the number of particles is constant, and surface area is only created by particle growth. We know that this will not be the case since experience shows that there can be a limited amount of auto-flocculation and N_p can decrease. However, this addition policy ensures that it is possible to maintain θ well below 100% (experiments are of course needed to tell us how much below 100%), so that even if some autoflocculation occurs, this will not lead to the accumulation of TN in the aqueous phase. Also, as we shall see later, it turns out that autoflocculation will stop as θ approaches 100% when only non-ionic surfactant is used, which means that we can maintain a control over N_p. The aim of this procedure is to keep the system in an auto-regulated state, which will allow us to obtain the required distribution of large particles.

Detailed recipes for all the runs of this series of experiments are given in the Appendix at the end of this paper, however, some of the experimental conditions are summarised in tables throughout the text in order to facilitate the reading of the paper. The main characteristics at the end of each stage for the latices made in runs presented in this section are summarised in Table 8. These include the polymer content (PC), the results of the Lo-C measurements of particle size, and the final surface coverage (θ_F). In the middle of the table there is a column called 'θ applied'. This parameter indicates the theoretical percent of the created surface area that will be covered by the non-ionic surfactant (TN) added during the semi-batch growth stage. The column labelled '$\theta > 100\%$' indicates whether or not the surface coverage exceeded 100% at least once during the semi-batch. 'Q_{TN}: cst' refers to the experiment where TN was added at a constant, rather than variable flow rate. Finally, methacrylic acid was added during the semi-batch stage of E2.329 at a concentration of 2% by mass with respect to total monomer.

3.2.1. Impact of the profile of addition of TN

Since no additional stabilisation is provided by the initiator or functional monomers in these runs (except for E2.329), the profile of addition of TN is essentially the only parameter available for the control of the PSD. Fig. 8 presents the evolution of the number of particles for runs E2.310 and E2.314, and Fig. 9 the evolution of the surface

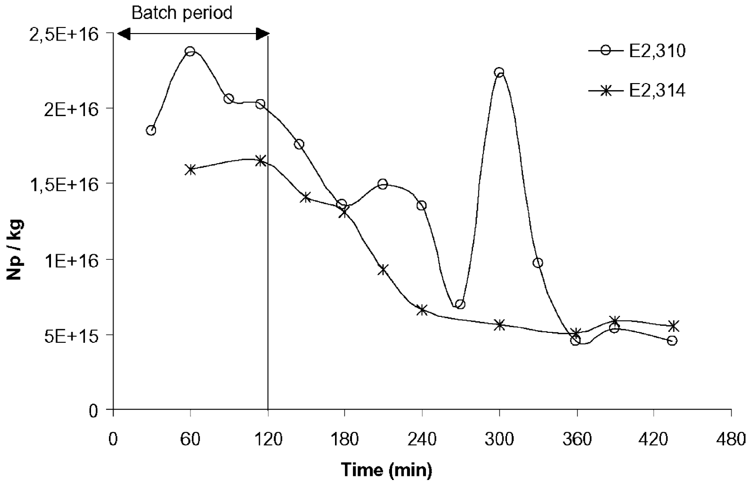

Fig. 8. Effect of the mode of addition of TN on N_p for runs E2.310 and 2.314.

coverage and the polydispersity index as a function of the reaction time. The surfactant is added differently for these runs. For E2.310, TN is added at a constant flow rate, while it is added according to a profile of addition for E2.314 as shown in Table 9.

In the case of E2.314, one observes a progressive decrease of N_p for the first half of the experiment until it levels off at a constant value for the remaining four hours. N_p remains constant since the surface coverage reaches a stable value as it can be seen from Fig. 9. The evolution of the polydispersity index (I_p) provided by Malvern Lo-C is also shown in Fig. 9. If $I_p > 0.1$, it can no longer be assumed that the latex is monodisperse, and the analysis of the results based on a measurement of d_p must be viewed with caution (circled points in Fig. 9). An increase in I_p can be caused by either the nucleation and stabilisation of small particles, or coagulation of some of the particles present in the system (these can of course occur simultaneously). A decrease in the average particle diameter reflects the appearance of smaller particles even if this renucleation cannot be quantified by such measurements, whereas coagulation will result in a larger average d_p. Renucleation is observed between 180 and 240 min during run E2.310, and again between 270 and 330 min. Given that I_p is relatively high for these points, the value of the calculated surface coverage is not reliable (it is quite likely too high). But, since no additional stabilisation is provided by the system, renucleation is followed by limited flocculation, which narrows the PSD and restores an adequate surface coverage. These results demonstrate that it is useful to add TN at a variable feed rate. Indeed, although the total amount of added TN is higher for E2.314 than for E2.310, no significant renucleation is observed during the semi-batch and the polydispersity index remains close to 0.1 throughout all the reaction. This indicates that the profile addition of TN is well adapted to the surface area growth. Indeed, since the particle surface area develops much faster at the beginning of the growth than at the end, adding surfactant a constant flow rate will

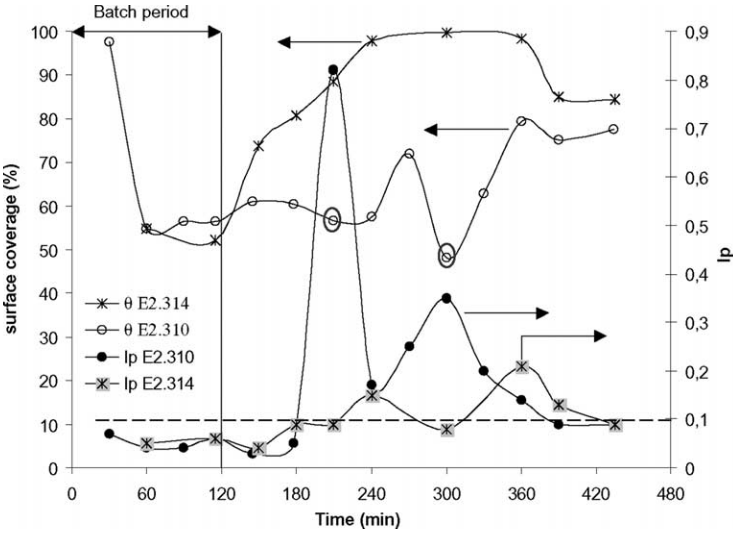

Fig. 9. Effect of the mode of addition on the evolution of the surface coverage for runs E2.310 and 2.314.

Table 9
Recipes for runs E2.310 and E2.314

Flow rate g/h	E2.310	E2.314
AscA batch	0.07	0.08
AscA semi-batch	0.22	0.25
Monomer	152	177
TN		
1st hour	1.87	4.04
2nd hour	1.87	3.21
3rd hour	1.87	2.80
4th hour	1.87	2.31
Total amount of TN (g)	8.41	12.37

lead to either an accumulation of TN at the end of the experiment, or a lack of stability during the early moments of the reaction. This phenomenon is reflected in the evolution of N_p for the run E2.310, that is why the renucleation phenomenon is observable for this run.

Fig. 10 shows the final PSD determined by SLS (Coulter LS 230) for both latices. The arrows on the graph indicate the size corresponding to the top of the peak but not the average size. For both latices we observe a bimodal PSD, with a small fraction of large particles (due to limited flocculation) near 1400 nm. These very large particles result from the limited flocculation of several smaller particles. As expected, the volume fraction of very large particles is slightly greater for E2.310, where the total amount of surfactant added was lower. The reason proposed to explain this is that in order to reach an adequate surface coverage more flocculation will occur since the amount of surfactant is lower. It is useful to underline the shortcomings of the technique used to measure the PSD up to this point: comparing Fig. 9 and Fig. 10 shows that the information provided by the fixed angle QELS method does not include the very large particles, most likely because these very large particles are not numerous and so have little impact on fixed angle PCS [15,16]. Nevertheless, despite this limited bimodality, it is very interesting to note the similarity of the PSD for these two experiments. Once again, we can see the self-regulating nature of the emulsion as the number and size of particles evolves toward similar values in both cases.

If we compare the main characteristics of the latices at the end of each stage for runs E2.315 and E2.323 (Table 8), it can be seen that the polymer content and the number of particles are lower for E2.323 than for E2.315 at the end of the batch stage. This is due to an inhibition period (30 min) during the batch stage of E2.323. Since the conversion was not monitored on-line, it was lower than expected when the semi-batch phase began, and the addition profile of TN was no longer correctly adapted. The evolution of the number of particles and the surface coverage as a function of time of E2.315 and E2.323 are compared in Fig. 11, as well as the evolution of the polydispersity index I_p.

Given that the PSD at the end of the batch period of E2.323 is not what was expected because of the inhibition period, the addition profile of TN during the semi-batch is not properly adapted. Thus, as can be seen in Fig. 11 the surface coverage increases to above 100% immediately following the beginning of the semi-batch stage. In addition, since there is more monomer during the early stages of the semi-batch period in E2.323, renucleation is favoured. A loss of control over the PSD during the semi-batch period occurs, and the final number of particles is slightly higher than expected ($1.5\times10^{16}\ \mathrm{kg}^{-1}$). This loss of control is reflected by the increase in I_p. Indeed, the stabilisation of new (smaller) particles makes the PSD broader ($I_p>0.1$). Obviously, a large part of the renucleation is homogeneous, but when $\theta>100\%$ the concentration of additional TN in the aqueous phase is quite likely higher than the CMC (its CMC is approximately 0.25 g/l H_2O), part of the renucleation could be micellar. This same behaviour was observed for other runs presented by Boutti [9], but not reported here for the sake of brevity.

On the other hand, the addition profile for E2.315 appears to be well-adapted, and no loss of control over the PSD is detected. The number of particles decreases progressively during the semi-batch until the stabilisation, and the

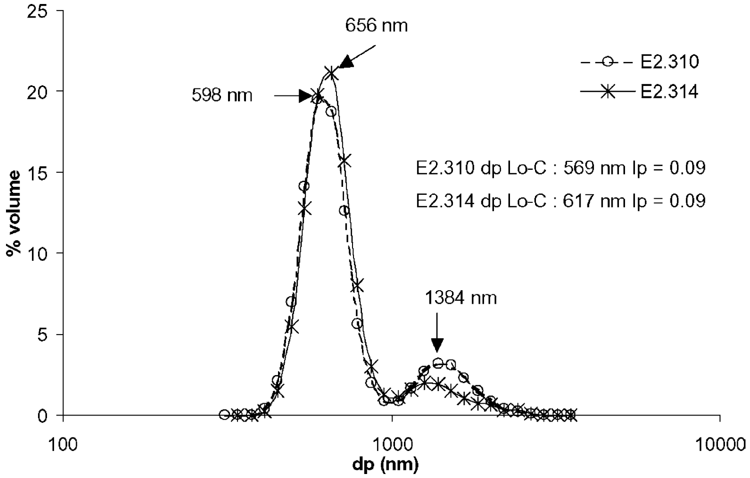

Fig. 10. Effect of the profile of addition of TN on the final PSD for runs E2.310 and 2.314.

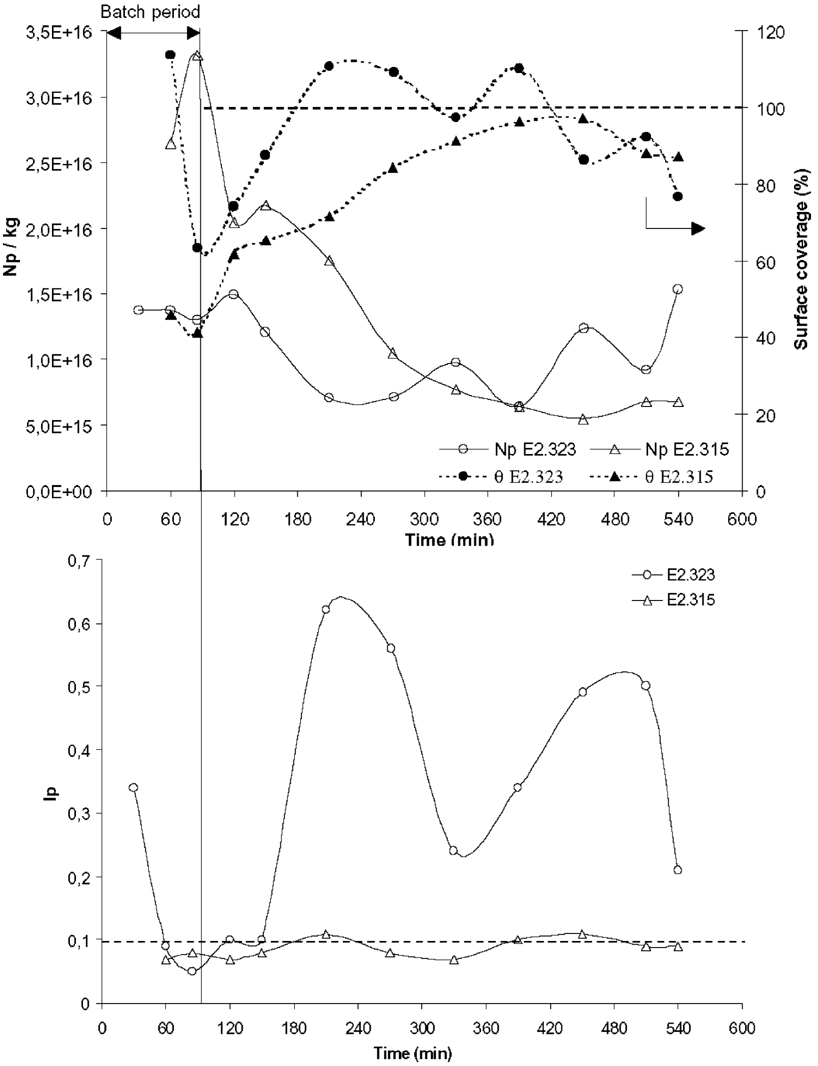

Fig. 11. Impact of an inadequate profile of addition of surfactant on the granulometry.

polydispersity index remains close to 0.1 during the entire reaction. Finally the PSD of E2.315 respects all the requirements previously described, and the results are essentially the same as for E2.314, in the sense that N_p remains stable since the surface coverage reaches a stable value. The main difference between E2.314 and E2.315 is the final polymer content as described below.

3.2.2. *Effect of the polymer content*

As we can see in Table 8, the final characteristics of the latices from runs E2.314 and E2.315 are similar except for the polymer content. Indeed, the PSD are fairly similar for both experiments, but the polymer content is higher for E2.315. This is due to the experimental procedure, which is described in Table 10. The batch period lasted 2 h for run E2.314 and 90 min for E2.315, and the neat monomer flow rate was 177 g/h for E2.314 and 101 g/h for E2.315 as indicated in Table 10. Fig. 12 shows the evolution of the PSD and the polymer content for these experiments as well as the viscosity as a function of the shear rate for the final latices.

As can be seen in Fig. 12, the results of these runs are very similar despite the difference in the experimental

Table 10
Experimental procedures for runs E2.314 and E2.315

Flow rate g/h	E2.314	E2.315
AscA batch	0.08	0.04
AscA semi-batch	0.25	0.14
Monomer	177	101
TN		
1st hour	4.04	2.40
2nd hour	3.21	1.98
3rd hour	2.80	1.77
4th hour	2.31	1.62
5th hour	–	1.52
6th hour	–	1.44
7th hour	–	1.36
Total amount of TN (g)	12.37	12.02

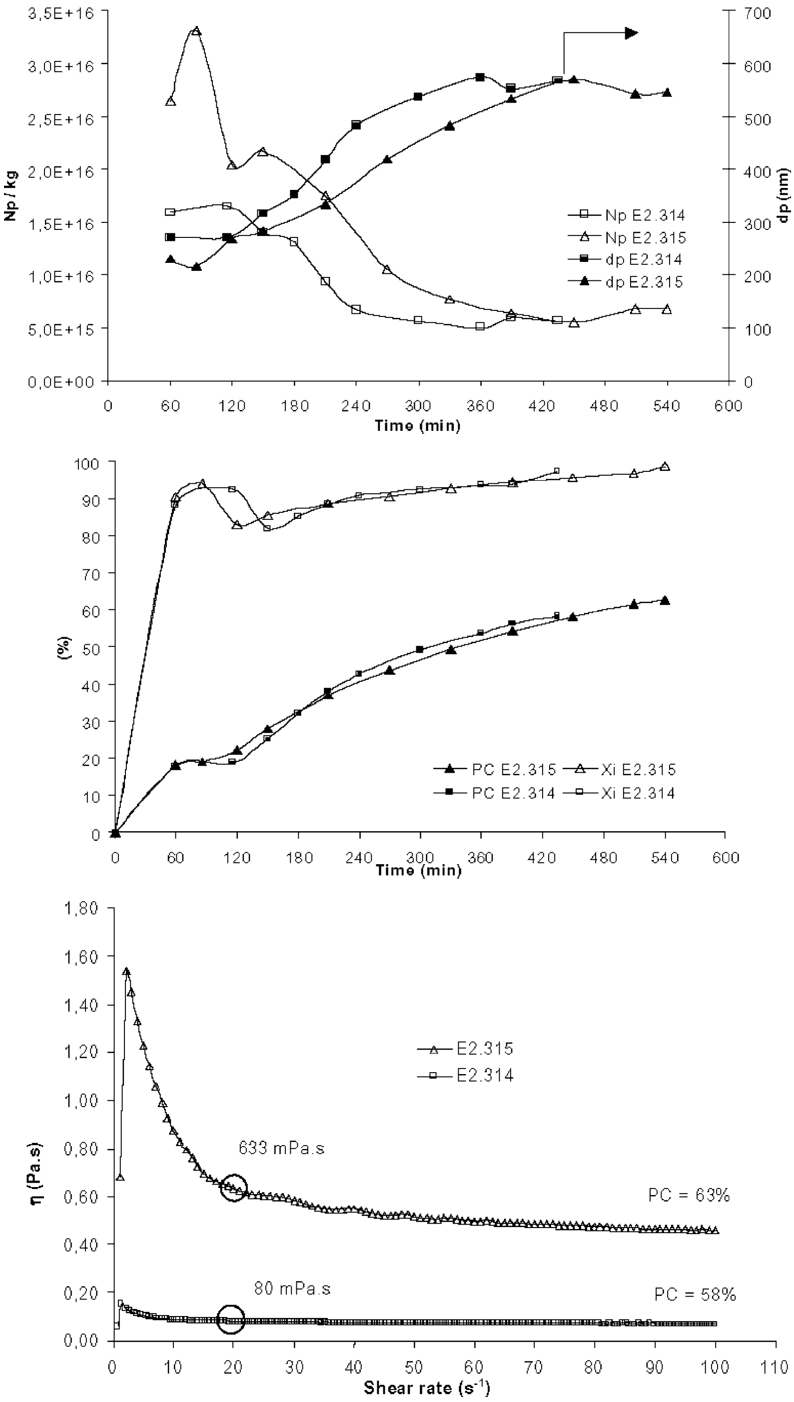

Fig. 12. Effect of the polymer content on the viscosity.

procedures. The PSD evolves in the same way throughout both polymerisations. More monomer is added in E2.315, so the final polymer content is higher, but the trajectories of N_p and d_p are not noticeably influenced by the prolonged addition. The impact of the polymer content on the viscosity appears clearly in the last graph presented in Fig. 12. If we compare the viscosity of these two latices for a shear rate of 20 s^{-1}, the viscosity is approximately eight times higher for E2.315 whereas the polymer content is only 5% higher. The sharp increase of the viscosity occurs since the latex is approaching the limiting volume fraction of polymer for a monomodal latex. This evolution of the viscosity underlines the sensitivity of this parameter and confirms that these products behave as if they had a monomodal PSD (at least from the point of view of the viscosity).

3.2.3. Reproducibility and robustness

In this study some parameters such as the duration of the

Table 11
Experimental procedures for runs E2.38 and E2.39

Flow rate g/h	E2.38	E2.39
AscA batch	Shots (0.025 g 35 min)	0.05
AscA semi-batch	0.15	0.15
Monomer	108	125
TN		
1st hour	2.18	2.18
2nd hour	1.79	1.79
3rd hour	1.59	1.59

batch period, the flow rates of monomer and AscA were modified from a run to another in order to refine our knowledge on the process. However, it also allows us to demonstrate the degree of reproducibility and the robustness of the process.

Once again, the characteristics of the latices E2.38 and E2.39 are shown in Table 8. For these runs the only difference is the way in which AscA is added during the batch period. As shown in Table 11 AscA was added by shots for E2.38, while it was added continuously for E2.39. Fig. 13 presents the evolution of the PSD and the conversion versus reaction time and Fig. 14 presents the final PSD obtained for these runs.

In so far as the kinetics are concerned, high conversions are reached earlier for run E2.39 in the batch period. Indeed, as was shown by Boutti et al. [9,12], the continuous addition of AscA leads to faster kinetics than addition by shots. During the semi-batch phase the solution of AscA is added continuously at the same flow rate for both experiments, and the evolution of the conversion is similar for both runs. Also, as can be seen from Figs. 13 and 14, the PSD is well controlled and very reproducible for both runs.

The PSD provided by SLS is in agreement with the one provided by PCS ($d_p = 545$ nm for the two latices vs. 560 nm for both using QELS at 90°), and it is very reproducible. We do not observe a tail near the very large sizes for E2.38. A hint of a peak around 1500 nm can be discerned for E2.39, but for all intents and purposes, this can be ignored. Note that the polymer content of these runs (E2.38 PC = 46 wt%, E2.39 = 48 wt%) is lower than in the experiments presented previously (E2.314 PC = 58 wt%,

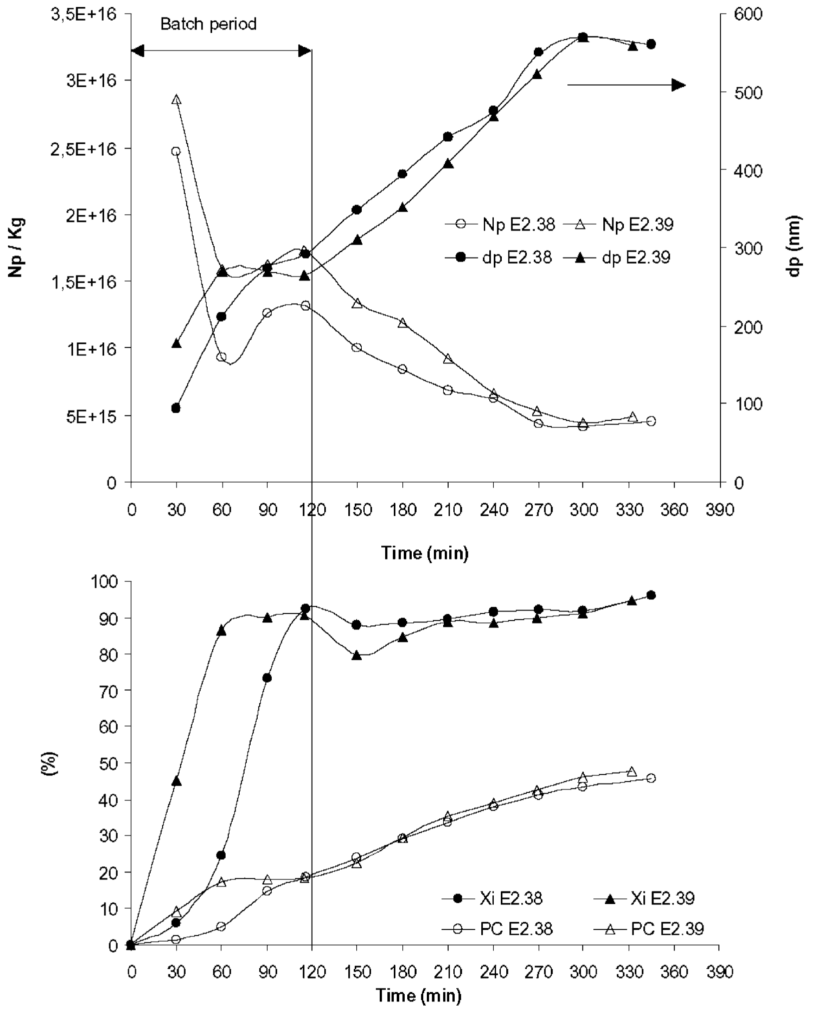

Fig. 13. Reproducibility of the process for the evolution of the PSD and the kinetics of runs E2.38 and E2.39.

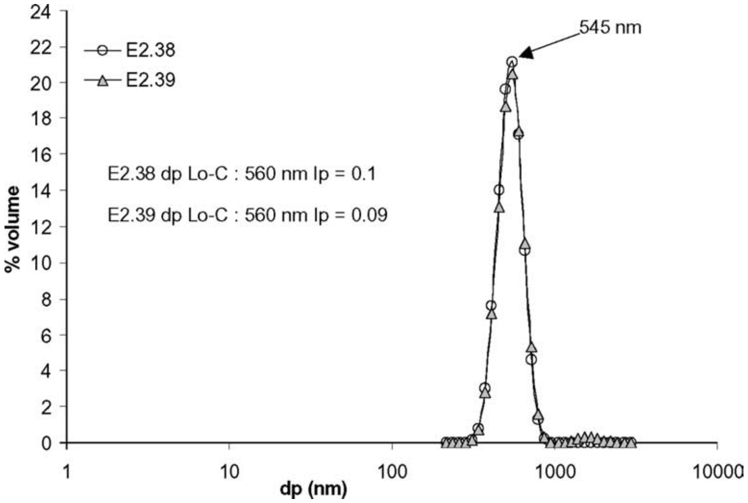

Fig. 14. Reproducibility of the final PSD determined by SLS (Coulter LS230).

E2.310 PC = 61 wt%). As we will see in detail below, when the polymer content increases, the surface coverage needed for the stabilisation is slightly higher. Thus, limited flocculation continues for a longer time, and this quite likely leads to the formation of larger particles observed for the runs E2.314 and E2.315.

Runs carried out according to different experimental procedures are presented in Table 8. Except for the duration of the batch period, the most important difference between these runs is that for run E2.329 the monomer mixture contained 2 wt% of methacrylic acid. The different experimental procedures are summarised in Table 12, and Fig. 15 presents the evolution of the average particle diameter as a function of the reaction time for these runs.

As can be seen from Fig. 15, despite the differences in the experimental procedures the evolution of the PSD as a function of time is similar for all these runs. Moreover, the incorporation of the methacrylic acid in the recipe does not lead to a modification of the PSD with respect to the other experiments. Indeed, as can be seen from the evolution of N_p and θ in Fig. 15, the PSD is controlled throughout all the polymerisation and E2.329 behaves like the others. The difficulty with functional monomers such as MAA is that since they are highly water-soluble, the formation of water-soluble stabilising molecules is favoured. However, because the pH of the latex in its normal state is between 2 and 3, we are below the p*K*a of MAA and any water-soluble PMAA chains should not be in an ionic state, which limits the stabilising effect. The low pH of the latex is the most probably due to the presence of acidic components from the reaction chain between ascorbic acid and hydrogen peroxide. Finally, these observations show the robustness of the process.

3.2.4. Determination of the stability zones

Given that the surface coverage is the main parameter in the control of the PSD, it is important to understand how it evolves during the synthesis of the first population of particles. Fig. 16 shows the evolution of θ as a function of the polymer content of the successful experiments.

As explained above, the aim of the proposed process is to keep the system in an auto-regulated state in so far as the stabilisation of the latex is concerned. As it can be seen in Fig. 16, the limited flocculation of particles during experiments pushes the surface coverage by TN to approximately 80–95% as the polymer content increases. Thus, this evolution of the surface coverage corresponds to the stabilisation required by the system as a function of the polymer content. When the surface coverage exceeds the

Table 12
Experimental procedures for runs E2.327 to E2.330

Flow rate g/h	E2.327	E2.328	E2.329	E2.330
AscA batch	0.06	0.04	0.04	0.06
AscA semi-batch	0.23	0.23	0.23	0.27
Monomer	148	154	165	163
TN				
1st hour	3.42	3.42	3.46	3.38
2nd hour	2.74	2.74	2.77	2.67
3rd hour	2.35	2.35	2.37	2.33
4th hour	2.15	2.15	2.17	2.13
5th hour	2.05	2.05	2.07	1.98

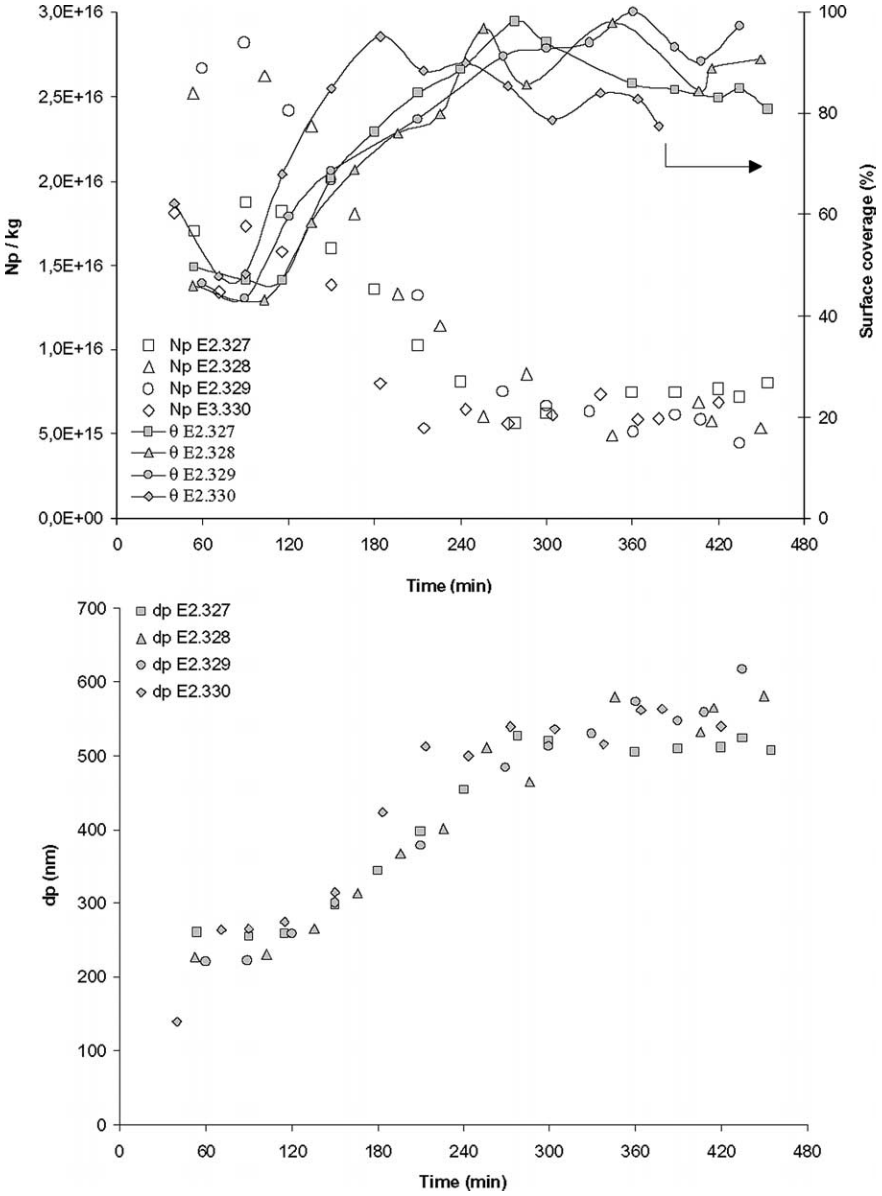

Fig. 15. Robustness of the process for the PSD.

upper limit of this band, especially if it exceeds 100%, renucleation occurs, and the newly formed particles are stabilised, which pushes θ to within the band shown in Fig. 16. Below the band shown in this Figure, under-stabilisation pushes the particles to coalesce, which causes the system to readjust itself until θ is once again in the 'stability zone'. Similar results have been reported in the literature, especially for electrostatically stabilised systems. For example, Sajjadi [21] studied the nucleation and stabilisation of BA polymerised with SDS and KPS in seeded emulsion systems at an original solid content of 33% (w/w) under starved conditions. He observed that particle formation could occur under monomer starved conditions if the surface coverage of the seed particles was above 55 ± 5%, and observed the creation of a θ bimodal latex under certain feed conditions. In an earlier study on the seeded emulsion polymerisation of vinyl acetate and methyl acrylate, Urquiola et al. [22] observed similar results for these more hydrophilic monomers and a commercial anionic surfactant ($C_{16}H_{29}O_7SNa$). In their case, secondary particle stabilisation was observed at a surface coverage over 68%. These results imply that the anionic surfactant is partitioned between the surface and aqueous phases, and that it is not necessary to be over the CMC in order to experience secondary nucleation. Sajjadi [21] also observed that if the surface coverage of the seed dropped below 25 ± 5%, the seed particles would begin to coagulate. Sajjadi and Brooks [23,24] also demonstrated that the quantity of monomer present during particle formation can have a striking impact on the number of particles nucleated, and in the presence of monomer droplets, significant numbers of new particles can be formed, leading to bimodal PSD. It

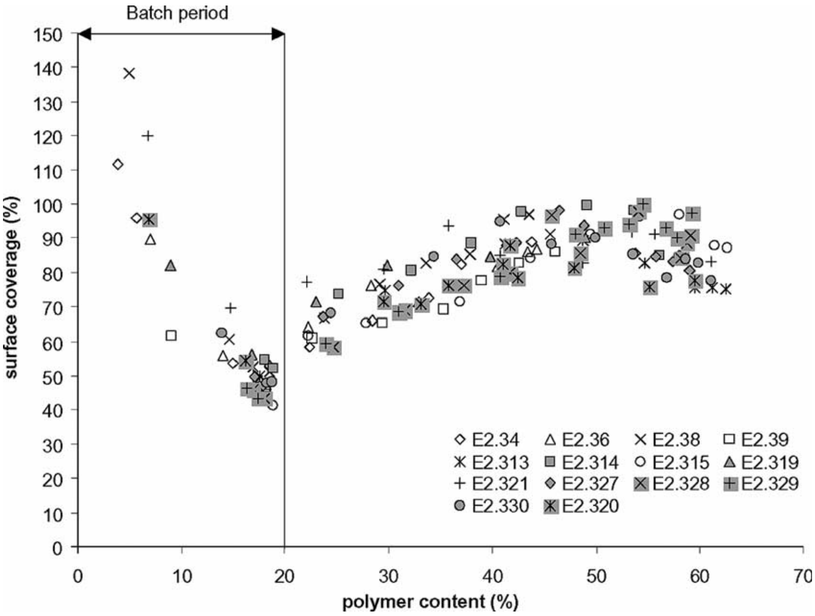

Fig. 16. Stability zones: surface coverage as a function of polymer content.

should be noted that the studies just cited were performed for lower monomer concentrations, with electrostatically stabilised systems and persulphate initiators, so the limits of stability are obviously different.

The results in Fig. 16, combined with the studies cited above suggest that there is a ‘stability’ band inside which particles generated by homogeneous nucleation are not stabilised, and flocculate onto large ones already present. Outside of this zone if there is an excess of surfactant we can easily renucleate particles and stabilise them. On the other hand, if the surface coverage is inadequate, the particles will flocculate, and push the system back into this band. This also implies that if one operates simply above the ‘stability band’, it might be possible to generate a certain number of small particles in the presence of larger ones, without destabilising the latex.

4. Conclusion

The results of this paper show that the key to reproducibly synthesising a concentrated latex with a well-controlled monomodal PSD is the control of secondary nucleation. Two main procedures have been tested in this work, one using APS as initiator and the other one using the redox couple H_2O_2/AscA.

First, it was shown that the negative charges provided by APS favour the undesirable stabilisation of homogeneously nucleated particles. However, these results suggest that when we want to create and stabilise small particles, i.e. in the last step of the process, this system will probably be better suited to the task, and this idea will be exploited in Part II of this work [7].

It was then shown that it is possible to synthesise a highly concentrated monomodal latex for use in producing HSC/LV latices was through the use of a combination of a HPO/AscA initiation system plus a stabilisation system rich in non-ionic surfactant. The process developed here allows us to produce an initial population of particles that respects the conditions required in the introduction. Moreover, this process is highly reproducible and robust. Even noticeable differences in the experimental procedure (other than varying the flow rate of surfactant) do not have a strong influence on the final PSD. The feasibility of the process has also been verified for a mixture of monomer composed by 2 wt% of methacrylic acid. Above all we saw that the correct adjustment of the addition of non-ionic surfactant during the semi-batch step allows us to maintain the process inside a clearly defined stability zone, and to achieve solid contents of about 60% (v/v) with large particles on the order of 550–650 nm in diameter. This type of stabilisation and the means of adding TN provide very reproducible control over the PSD, and adding functional monomer (MAA) under these conditions does not change the polymerisation behaviour.

These experiments show that the absence of additional stabilisation provided by the charges due to the initiator allows us to control the PSD. Indeed, with such a system, although homogeneous renucleation occurs it does not pose a problem. The shape of final PSD depends only on the rate of addition of the non-ionic surfactant. The addition of non-ionic surfactant during the semi-batch stage according to a calculated profile allows us to create conditions where the system becomes ‘self-regulating’. We can therefore avoid the stabilisation of homogeneously nucleated particles, and at the same time assure the stabilisation of a sufficient number of particles issued from the batch nucleation phase to satisfy the objectives laid out for this population.

Moreover, the limited flocculation improves the kinetics with respect to systems where this does not happen. Even though optimisation of the kinetics was not considered here, we nevertheless succeeded in synthesising a latex with a polymer content of about 60% with a total reaction time of 7 h (E2.314). For comparison, Schneider et al. [8] needed more than 10 h to reach 50% polymer content with the same components and similar final d_p.

This process was therefore adopted for the synthesis of the first population. At the end of this stage the latex is composed of a first population of particles with an average diameter about 550–650 nm (with a tail near the very large sizes). The polymer content is about 60%. The stability is provided in vast majority by the non-ionic surfactant (wt%TA $<0.1\%$) and the average surface coverage is 80–95%. In the next stage of the process, the objective is to create in situ an adequate second population of small particles without destabilising the latex and in a reproducible manner. This will be discussed in Part II [7].

Appendix A. Recipes used in the polymerisations initiated by HPO/AscA

All the experiments are carried out at 70 °C and the agitation speed is decreased when the polymer content increases in order to avoid coagulation due to enhanced particle collisions. For example when PC$>$55%: agitation speed <150 rpm. Feed flows are indicated in g/h.

Feed durations are indicated in minutes. Neat monomer corresponds to a composition containing 80 wt% of BuA and 20 wt% of MMA. For the surfactants the amounts indicated correspond to the global quantity added, but the active matter represents only 65 wt% for TN and 32 wt% for TA.

Table A1. Runs E2.31–E2.310

	E2.31	E2.34	E2.35	E2.36	E2.37	E2.38	E2.39	E2.310
Batch stage								
Duration	90	180	180	120	120	120	120	120
Water	889	375	376	389	407	392	390	386
BuA	80	80	80	80	80	80	80	80
MMA	20	20	20	20	20	20	20	20
TN (65%)	5.3400	2.6560	2.6837	2.8294	2.8031	2.7373	2.6516	3.5012
TA (32%)	0.0474	0.0288	0.0231	0.0226	0.0209	0.0225	0.0196	0.0239
H_2O_2	2	1	1.2	1	1	1	1	2.9
AscA solution								
AscA	0.5	1	1	1	1	1.5	1	1
Water	9.5	39	39	39	39	58.5	39	39
Flow rate	0.5	1.3	1.3	2	1.2	1.3	2	2.8
Semi-batch stage								
Neat monomer								
Feed flow	35.5	54	108	108	120	108	126	152
Feed duration	120	300	170	165	180	180	180	270
Ascorbic acid solution								
AscA	0.5	1	1	1	2	1.5	1	1
Water	9.5	39	39	39	38	58.5	39	39
Feed flow	0.5	3	3	6	3.3	6	6	8.5
Feed duration	120	300	170	165	180	180	180	270
Non-ionic surfactant solution								
TN (65%)	–	20	20	20	29.2	30	20	28.6
Water	–	98	100	100	51.4	150	100	75.5
Feed flow of TN solution								
1st hour	–	12	25.3	25.3	12.8	20.2	20.2	10.4
2nd hour	–	10.8	20.7	20.8	10.3	16.6	16.6	10.4
3rd hour	–	9.6	15	14	9.1	14.7	14.7	10.4
4th hour	–	9	–	–	–	–	–	10.4
5th hour	–	8.4	–	–	–	–	–	–
6th hour	–	–	–	–	–	–	–	–
7th hour	–	–	–	–	–	–	–	–
Finishing period	–	–	40	45	30	45	30	45
Final characteristics								
PC (%)	Coagulum	44	47	44	48	46	48	61
$\theta >$ 100%	–	No	Yes	No	Yes	No	No	No
d_p (nm)	–	490	411	444	538	560	560	617
I_p	–	0.09	0.22	0.10	0.70	0.10	0.09	0.09

Table A2. Runs E2.311–E2.318

	E2.311	E2.312	E2.313	E2.314	E2.315	E2.316	E2.317	E2.318
Batch stage								
Duration	120	120	120	120	90	90	60	120
Water	385	383	389	378	391	392	530	394
BuA	80	80	80	80	80	80	80	80
MMA	20	20	20	20	20	20	20	20
TN (65%)	3.0593	2.9417	3.0211	3.0046	3.0570	3.0545	4.3074	3.0884
TA (32%)	0.0219	0.0255	0.0242	0.0263	0.0222	0.0229	0.0300	0.0207
H_2O_2	2.8	2.8	5.9	4.9	2	2	3.5	2.5
AscA solution								
AscA	1	1	1	1	2	2	2	2
Water	39	39	39	39	38	38	38	38
Flow rate	2.8	2.8	2.8	3.3	1	1	1.7	1.3
Semi-batch stage								
Neat monomer								
Feed flow	151	151	152	177	101	101	181	136
Feed duration	240	480	330	270	420	280	300	300
Ascorbic acid solution								
AscA	1	1	1	1	2	2	2	2
Water	39	39	39	39	38	38	38	38
Feed flow	8.4	8.4	8.4	9.8	2.8	2.8	5	3.8
Feed duration	260	480	360	315	433	280	330	300
Non-ionic surfactant solution								
TN (65%)	23	42	19	20.6	45	45	30	25
Water	62	245	57.5	158	65	65	59	51
Feed flow of TN solution								
1st hour	17.8	41.3	18.0	54.0	9.0	9.0	20.3	15.4
2nd hour	17.8	36.3	13.7	42.9	7.5	7.5	16.5	12.2
3rd hour	17.8	33.0	12.0	37.5	6.7	6.7	14.5	10.6
4th hour	17.8	30.8	10.9	30.9	6.1	6.1	12.9	9.7
5th hour	–	28.9	10.1	–	5.7	5.7	11.9	9.0
6th hour	–	27.5	9.5	–	5.4	–	–	–
7th hour	–	26.3	–	–	5.1	–	–	–
8th hour	–	25.2	–	–	–	–	–	–
Finishing period	35	–	30	45	30	5	30	30
Final characteristics								
PC (%)	56.4	63.7	62	58	62.6	53	61	62
$\theta >$ 100%	Yes	Yes	No	No	No	Yes	Yes	Yes
d_p (nm)	480	430	570	569	547	515	455	486
I_p	0.13	0.50	0.12	0.09	0.09	0.27	0.17	0.31

Table A3. Runs E2.319–E2.328

	E2.319	E2.320	E2.321	E2.322	E2.323	E2.324	E2.327	E2.328
Batch stage								
Duration	60	150	90	90	90	150	120	105
Water	392	389	390	389	392	393	393	393
BuA	80	80	80	80	80	80	80	80
MMA	20	20	20	20	20	20	20	20
TN (65%)	3.1048	2.7746	3.0512	3.1300	3.0572	2.6930	2.7408	2.8685
TA (32%)	0.0234	0.0294	0.0216	0.0223	0.0232	0.0281	0.0307	0.0314
H_2O_2	2.5	2.5	2.7	4	1	1.5	1.7	1.7
AscA solution								
AscA	2	2	2	2	2	3	3	3
Water	38	38	38	38	38	57	57	57
Flow rate	1.2	1.2	2.5	2.5	0.9	0.5	1.1	0.9
Semi-batch stage								
Neat monomer								
Feed flow	135	134	134	134	101	90	147	154
Feed duration	180	315	320	310	420	420	315	310
Ascorbic acid solution								
AscA	2	2	2	2	2	3	3	3
Water	38	38	38	38	38	57	57	57
Feed flow	3.7	3.7	3.7	3.7	2.8	2.5	4.6	4.6
Feed duration	180	335	330	320	450	440	320	315
Non-ionic surfactant solution								
TN (65%)	23	25	25	25	45	50	50	50
Water	47	72	72	65	45	118	330	330
Feed flow of TN solution								
1st hour	15.3	16.8	16.9	16.5	9.0	13.2	40.0	40.0
2nd hour	11.7	13.5	13.6	13.3	7.5	11.2	32.0	32.0
3rd hour	10.2	11.9	12.0	11.7	6.7	10.0	27.4	27.4
4th hour	–	10.8	10.9	10.7	6.1	9.2	25.1	25.1
5th hour	–	10.1	10.1	9.9	5.7	8.6	24.0	24.0
6th hour	–	–	–	–	5.4	8.1	–	–
7th hour	–	–	–	–	5.1	7.8	–	–
Finishing period	–	20	10	10	30	20	20	35
Final characteristics								
PC (%)	49	61.5	61	61	63.5	60	59	59
$\theta > 100\%$	No	No	No	Yes	Yes	Yes	No	No
d_p (nm)	478	553	534	416	423	483	507	580
I_p	0.04	0.10	0.15	0.65	0.21	0.22	0.12	0.12

Table A4. Runs E2.329–E2.330

	E2.329[a]	E2.330
Batch stage		
Duration	90	120
Water	393	394
BuA	80	80
MMA	20	20
TN (65%)	2.8786	2.7903
TA (32%)	0.0299	0.0294
H_2O_2	1.7	1.8
AscA solution		
AscA	3	1
Water	57	39
Flow rate	0.8	2.3
Semi-batch stage		
Neat monomer		
Feed flow	165	163
Feed duration	318	260
Ascorbic acid solution		
AscA	3	1
Water	57	39
Feed flow	4.6	10
Feed duration	325	285
Non-ionic surfactant solution		
TN (65%)	50	20
Water	330	78
Feed flow of TN solution		
1st hour	40.0	25.5
2nd hour	32.0	20.1
3rd hour	27.4	17.6
4th hour	25.1	16.1
5th hour	24.0	14.9
6th hour	–	–
7th hour	–	–
Finishing period	27	40
Final characteristics		
PC (%)	59	60
$\theta > 100\%$	No	No
d_p (nm)	618	540
I_p	0.11	0.12

[a] For E2.329 the neat monomer added during the semi-batch stage is composed of 78 wt% of BuA, 20 wt% of MMA and 2 wt% of MAA.

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