

High solids content emulsion polymerisation without intermediate seeds. Part II. In situ generation of bimodal latices

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Abstract

A process for the production of high solid content latexes with low viscosity that does not require the use of intermediate seeds is developed. It is shown that the second population of a bimodal latex can be generated by controlled homogeneous nucleation through the use of a combination of an initiator that generates charged free radicals and a mixed surfactant system that is very rich in non-ionic surfactant. The process was shown to be reproducible, and was used to produce a latex with a solid content of almost 77% (v/v) and a viscosity of 1.5 Pa s at a shear rate of 20 s⁻¹.

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1. Introduction

As mentioned in Part I of this series of papers [1], the ultimate objective of this work is to develop a robust and reproducible process for the preparation of High Solid Content Latices with Low Viscosities (HSC/LV) without the use of intermediate seeds. By high solid contents, we mean at least 70% by volume, and by low viscosity, we have chosen an upper limit of 1.5 Pa s at a shear rate of 20 s⁻¹. One of the most appropriate ways of achieving this objective is to use a well defined particle size distribution that is composed of two populations of particles, where the diameter of the larger particles is 4–8 times larger than that of the smaller one, and the larger particles represent 75–85% (v/v) of the polymer in the final product. A full discussion of the reasons for this choice are given in the literature, and the interested reader is referred to the review by Guyot et al. [2] for more information on this point. Briefly, it is necessary to create a bimodal particle size distribution to minimise particle–particle interaction, and one of the most important

issues is to generate small particles in the correct proportion and size range. Failing to do so, especially if one generates too many fines, or fines that are too small, will lead to an extremely high final viscosity.

The most logical means of producing a bimodal PSD is shown in Fig. 1, where it can be seen that a process will consist of four stages:

- Stage 1: the creation of a well-defined number of particles that will form the initial population.
- Stage 2: the concentration of this initial population of particles to approximately 60% solids.
- Stage 3: the introduction of a second population of particles into the first population.
- Stage 4: the concentration and parallel growth of the two populations.

Broadly speaking, there are two families of processes available for making such bimodal PSDs, and these processes differ essentially at the level of Stage 3. These two families of processes are: (1) blending two seeds, and then concentrating them to the desired solid content; (2) the creation of small particles in the presence of an initial population of larger ones. The first alternative works, and has been the object of a number of patents (summarised in

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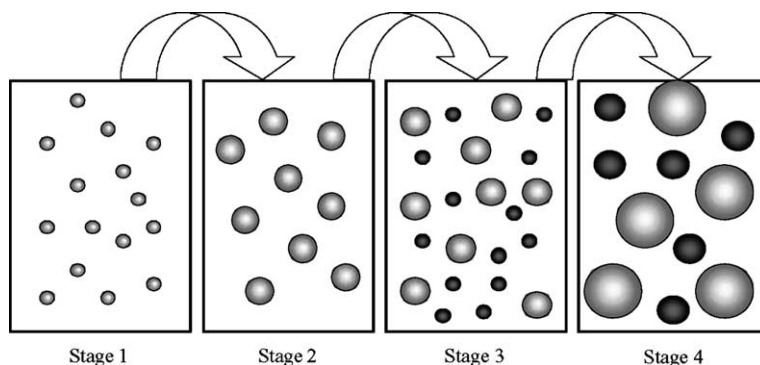


Fig. 1. Schema of a process for the creation of a HSC/LV bimodal latex.

[2]) and academic studies [3,4]. However, as mentioned in Part I, this is not a particularly desirable route to increasing the solid content as the use of intermediate seeds is costly, and requires additional reactions, as well as storage and handling steps. It is therefore useful to take the second route, and create a bimodal PSD in situ. However, this presents a number of challenges. For instance, it has been shown that the use of shots of initiator, monomer and/or surfactant to create the second population is often difficult to master, and can lead to the partial (or total) destabilisation of the system. To the best of our knowledge, the highest solid content attained in this manner was 68% (v/v) by Schneider et al. [3]. They managed to make a latex with a bimodal (or trimodal) PSD, but the lowest viscosity they managed to attain was approximately 2.5 Pa s at a shear rate of 20 s^{-1} . In addition they reported problems of reproducibility and loss of stability related to an extremely rapid generation of the small particles by shot addition.

Stages 1 and 2 were addressed in Part I [1], and in the current work we will focus on developing a robust and reproducible means of generating the second population of particles (i.e. doing Stage 3 in situ), and explore several strategies for doing so. Very briefly, it was demonstrated in Part I that the use of an electrically neutral initiation system (hydrogen peroxide/ascorbic acid), combined with the use of a feed of TN to keep surface coverage at approximately 85% and a small amount of anionic surfactant in the initial charge allowed us to produce a monomodal latex of large particles ($d_p > 500 \text{ nm}$) at solids contents of up to 60% (v/v) [1]. This allowed the system to become 'self-regulated', in the sense that the creation of too many particles led to a controlled flocculation, and thus a reduction of the surface area, and an overstabilisation led to the creation of new particles, and therefore an increase in the surface area of the latex.

In this paper, we will concentrate on developing a procedure for the renucleation of the second population, and pay particular attention to the role of the initiator in the renucleation step. An initial study was carried out using $\text{H}_2\text{O}_2/\text{AscA}$ as the initiator, and a second one using APS, each using different experimental procedures.

2. Experimental

The monomers used in this study were methylmethacrylate (MMA) and butyl acrylate (BA). The copolymers always contained 20% by weight MMA, and 80% by weight BA. 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 group 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 the results of their characterisation were presented elsewhere [5].

The concentrated intermediate latices used here (i.e. the population of large particles) were produced as described in Part I (in fact, some of the latices described therein were used in the previous study, so particular attention is paid to keeping the same nomenclature) [1].

Since the anionic surfactant used in this work is an efficient nucleation agent [1,6], it is logical to use it to generate the second population. In addition, it was shown in a parallel paper from this group that this same surfactant is strongly partitioned between the surface of the particles and the aqueous phase, so care must be taken in using it to create the population of small particles [7].

Four different experimental procedures described below were tested for the creation of the secondary particles in the presence of the larger ones.

2.1. Procedure no 1 (Runs E3.1, E3.2, E3.3 and E3.4)

The first population is purged with nitrogen and heated to $70 \text{ }^\circ\text{C}$ after addition of a small amount of hydrogen peroxide. The reaction is then begun with the addition of AscA. At the beginning of the reaction, a shot of anionic surfactant solution is added to the reactor and the monomer intended for the creation of

Table 1
Detailed experimental procedure for runs E3.1 to E3.4

Run	First population	Added TA (g)	θ_i theoretical (%)	$\theta_{P30\%}$ (%)	AscA addition (g)	Added monomer (g)	Addition of monomer (min)
E3.1	E2.38	0.09	98.3	92.8	0.16	17.5	5
E3.2	E2.38	0.26	113.7	97.4	0.15	17.6	10
E3.3	E2.39	0.08	84.4	79.4	0.23	16.1	30
E3.4	E2.39	0.08	84.4	79.4	0.23	16.1	20

the second population is added quickly for a period of 5–30 min.

2.2. Procedure no 2 (Runs E3.7, E3.8)

The first population is purged with nitrogen, and swollen with monomer to a given level. A solution of anionic surfactant is then added along with a small amount of H_2O_2 . The reactor is heated to 70 °C, the reaction begins with the addition of AscA, and monomer is added continuously during the reaction.

2.3. Procedure no 3 (Runs E3.9, E3.10, E3.13)

The first population is purged with nitrogen and heated to 70 °C. The particles are swollen, and a solution of anionic surfactant and H_2O_2 are added. The reaction begins once again when AscA is added. Monomer and non-ionic surfactant are added continuously.

2.4. Procedure no 4 (E3.14)

The synthesis of the first population is done the day before the renucleation and the latex is stored overnight in the reactor. A solution of emulsifier composed of both anionic and non-ionic surfactants is added just before the polymerisation. The reaction begins with the addition of AscA, and monomer and non-ionic surfactant are added continuously.

Polymerisations were carried out in a three-litre glass reactor. The reactants (monomer, initiator and surfactant) are fed into the bulk of the latex by means of three lateral ports. The way in which the additional reagents are fed to the reactor is particularly important for the synthesis of HSC latexes. Indeed, since latexes are somewhat viscous (in an absolute sense), especially at the beginning of the renucleation stage, if the addition is done through the top of the reactor, the reactants are not homogeneously dispersed in the reaction mixture, and this can provoke severe problems, especially for the stabilisation. The solutions of surfactant and initiator are added using a syringe pump. The monomer mixture is added using either a syringe pump for flow rates lower than 200 ml/h, or a membrane pump for higher flow rates.

It should be noted that since the renucleation stage takes place after the growth of the first population, the first population was occasionally stored for a few days before

being used for renucleation study. However, these particles were not subjected to any modification, and the results obtained using the stored particles are the same as those obtained if the complete process is carried out without interruption (this was verified several times).

3. Results and discussion

3.1. Runs initiated with the HPO/AscA redox system

The use of the electrically neutral initiation system in the generation of the first population of particles helped to avoid the stabilisation of the homogeneously nucleated particles, and maintaining the surface coverage of the latex below an upper limit kept the system in a self-regulated state [1]. In other words, there was an insufficient level of stabilisation and the small particles formed in this manner flocculated onto the larger ones. Therefore, one possible means of creating the small particles in situ would be to alter these conditions to help favour the stabilisation of the homogeneously nucleated particles, and use them as the second population. Thus, the first series of experiments performed here dealt with the generation of the second population with essentially the same ingredients as were used for the first one, but in slightly different proportions.

3.1.1. E3.1–E3.4

These runs were carried out using Procedure no 1. The parameters modified for those experiments are the concentration of anionic surfactant added in the shot, and the flow rate of monomer as shown in Table 1. The amounts of surfactant and monomer added are indicated for 100 g of polymer in the first population throughout the entire chapter. The amount of AscA added is indicated relatively to 100 g of added monomer. Also, the name of the first population (see [1]) is specified, and ' θ_i theoretical' is the average surface coverage at the beginning of the renucleation period after the addition of the anionic surfactant solution assuming that all the surfactant is on the particle surface. $\theta_{P30\%}$ corresponds to the average surface coverage assuming that 70% of the added anionic surfactant remains available in the aqueous phase and that 30% is adsorbed on the particle surface (see [7]).

Boutti et al. [7] showed that for a system of very similar composition and a polymer content of 15%, it appeared that 70–80% of the anionic surfactant added remains available in

Table 2
Characteristics of the latexes at the beginning of the renucleation stage

Run	Beginning of the renucleation		
	PC _i (%)	d _p (nm)	I _p
E3.1	45	560	0.10
E3.2	45	560	0.10
E3.3	50	560	0.09
E3.4	50	560	0.09

the aqueous phase. Based on these results, the concentration of TA in water would correspond to $2 \cdot \text{CMC}_{\text{TA}}$ for these runs, except for E3.2 where it would represent $6 \cdot \text{CMC}_{\text{TA}}$. This is not entirely reasonable since it is unlikely from a thermodynamic point of view that we would form micelles in the presence of highly unsaturated surface. Given that the polymer contents in these experiments are significantly higher than 15% (in the order of 55–65% in the experiments reported here) we can consider that 70% of surfactant remaining in water is an upper limit, and under these conditions, the surface coverage will be between θ_i theoretical and ' $\theta_{P30\%}$ '. Also, it is equally probable that a fraction of TN is in the aqueous phase, so one cannot entirely exclude the possibility that mixed micelles are therefore present in the aqueous phase. For all the experiments reported in this section, the concentration of anionic surfactant is in the same range of values. Indeed, as will be discussed below, we chose to use a moderate concentration of TA (few times the CMC) because we want to do a 'gentle' renucleation in order to avoid destabilising of the system.

The main characteristics of the latexes before the renucleation period are presented in Table 2. The average particle diameter and I_p provided by Malvern Lo-C are indicated. It is obvious that these values are not reliable for the characterisation of bimodal latexes, so only the characterisation of the PSD using the Coulter LS-230 is reported here.

Fig. 2 shows the PSD determined by Coulter LS 230 (SLS—static light scattering) for the initial populations and after the renucleation period. Note that during the period that this work was done, it was not always possible for the authors to have access to the static light scattering equipment, so some of the characterisations were obligatorily done with QELS at an angle of 90° (Malvern Lo-C). Fig. 2 shows that there is no evidence of any small particles that were stabilised by the end of the four runs. On the contrary, the shoulder centred on 1000 nm

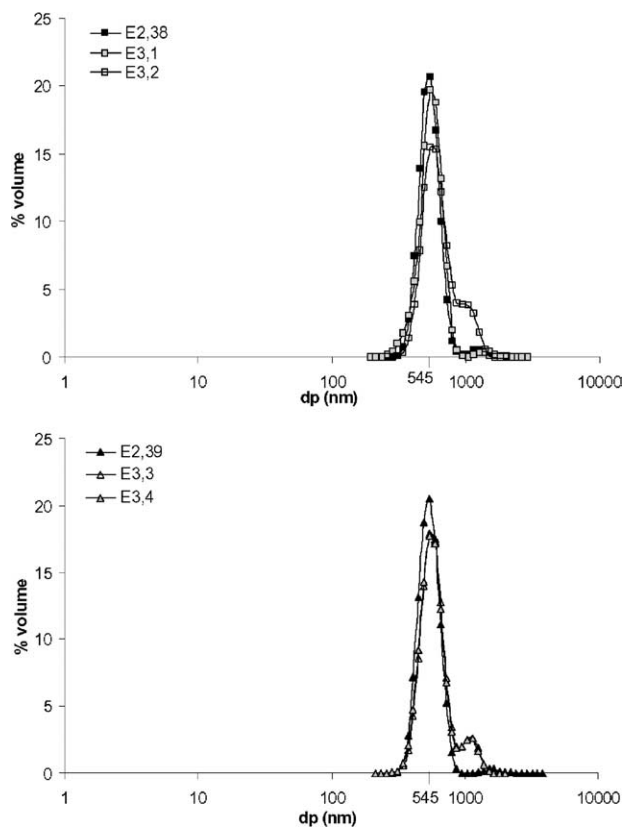


Fig. 2. PSD of the initial populations and after the renucleation stage determined by SLS (Coulter LS230).

suggests that a certain amount of controlled flocculation occurred during this step. New particles were probably created since it is known that homogeneous nucleation occurs with this system, and also a certain amount of TA is available in the aqueous phase. However, it seems that in these conditions, even for E3.2 where the amount of TA added is much higher, even if small particles are nucleated they are not stabilised.

The evolution of the number of particles during the reaction (calculated from particle diameter provided by QELS so the results should be viewed more as tendencies than absolute numbers) is similar for all these runs. Fig. 3 presents the evolution of N_p and $\theta_{\text{theoretical}}$ for E3.1. This figure suggests that renucleation took place but was followed by limited flocculation. As was the case in Part I [1], the system counterbalances the lack of stabilisation induced by the generation of new particles at around 60 min in the absence of a large excess of surfactant and of

Table 3
Detailed experimental procedure for runs E3.7 and E3.8

Run	First population	Added TA (g)	θ_i theoretical (%)	AscA addition (g)	Addition of monomer
E3.7	E2.312	0.06	89	0.13	First population swollen at 15% + 34.3 g/h
E3.8	E2.312	0.03	87	0.19	First population swollen at 15% + 34.5 g/h

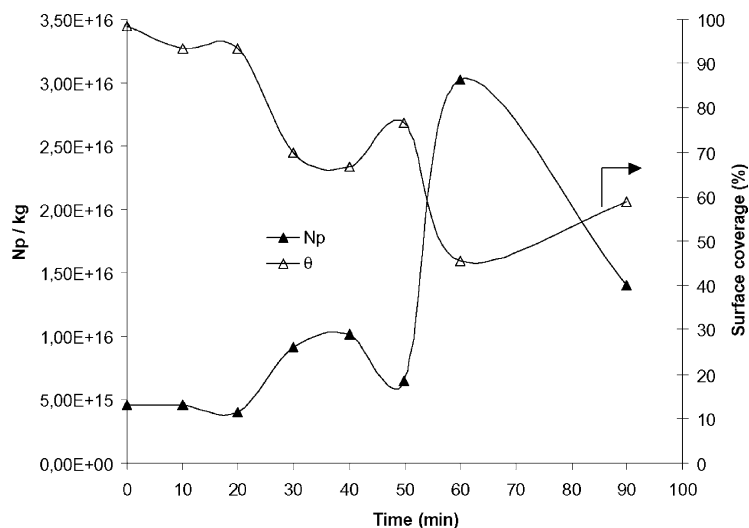


Fig. 3. Evolution of the surface coverage and the number of particles as a function of the reaction time for run E3.1.

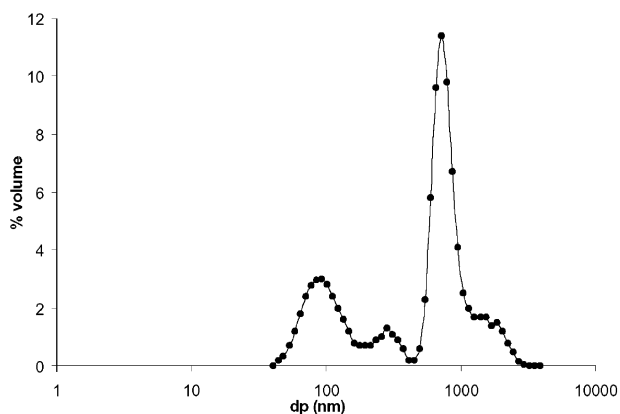


Fig. 4. PSD of the first population (E2.312) for runs E3.7 and E3.8 determined by SLS.

electrically charged end groups from the initiator by reducing the particle surface. The consequence is the appearance of very large particles, as shown in Fig. 2. Note that, after the shot of emulsifier and the addition of monomer, no additional reagents are added. Thus, after the limited flocculation no additional particles are formed and the PSD remains more or less fixed, but is broader than the original population due to the formation of some very large particles by limited flocculation.

The experimental procedure was therefore modified in an initial attempt to create a bimodal PSD by adding monomer continuously after the shot of surfactant. It is possible that

this would allow us to constantly create new particles in a controlled manner, and thus to stabilise a small population after the limited flocculation.

3.1.2. E3.7 and E3.8

E3.7 and E3.8 were carried out according to Procedure no 2, which is detailed in Table 3. The parameter that was modified here is the amount of anionic surfactant added. The first population of particles is swollen by monomer at 15 wt% with respect to the amount of polymer. Table 4 summarises the characteristics of the latexes at the beginning and the end of the renucleation stage.

Note that these experiments were carried out without a full characterisation of the intermediate latex for reasons explained above. Thus it happened that the full PSD of the first population was often available only after the renucleation experiments were carried out. Given these limitations it is not possible to draw any definite conclusions on the influence of the amount of anionic surfactant from the results of these experiments. First, and most importantly, this is because the latex flocculated. Second, it was realised after the fact that the PSD of the first population was inadequate. Post reaction characterisation showed that the addition profile of TN was inappropriate during the growth of the first population, so the surface coverage exceeded 100%, and the PSD was not well-controlled (cf. [1]). Thus, as we can see from the value of the polydispersity index before the renucleation stage (Table 4) and from Fig. 4 the PSD of E2.312 would

Table 4
Characteristics of the latexes at the beginning and the end of the renucleation stage

Run	Beginning of the renucleation			End of the renucleation stage		
	PC _i (%)	d _p (nm)	I _p	PC _F (%)	d _p (nm)	I _p
E3.7	55	487	0.5	Coagulum	–	–
E3.8	56	487	0.5	Coagulum	–	–

Table 5
Detailed experimental procedures for runs E3.9, E3.10 and E3.13

Run	First population	Added TA (g)	θ_i theoretical (%)	AscA addition	TN (g/h)	Addition of monomer
E3.9	E2.314	0.09	93	0.12	3	First population swollen at 10% + 63.5 g/h
E3.10	E2.314	0.09	93	0.41	3	First population swollen at 10% + 63.2 g/h
E3.13	E2.315	0.26	250	0.20	4.5	First population swollen at 5% + 75.9 g/h

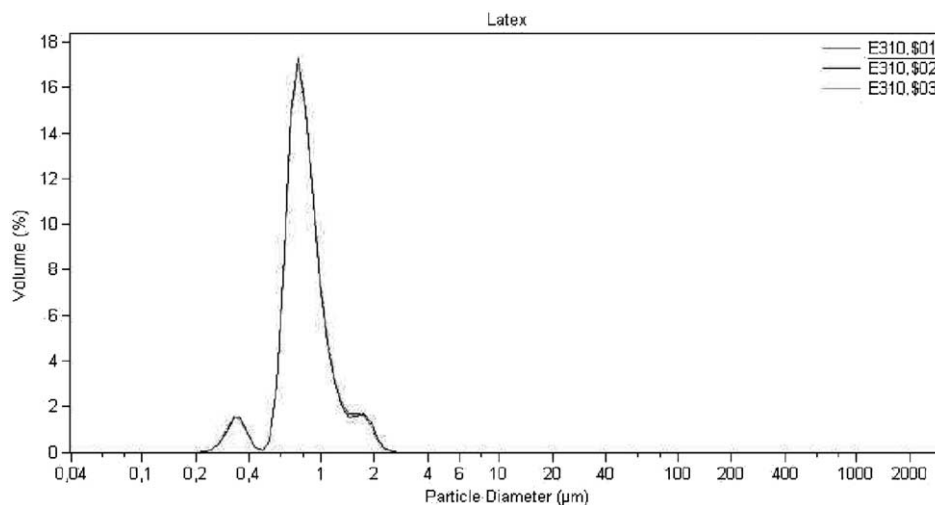


Fig. 5. PSD for the run E3.10 determined by SLS.

not have allowed us to understand the influence of the renucleation period in any event. This underlines the importance of controlling the PSD of the first population in order to understand and control the phenomena implicated in the renucleation stage. Nevertheless, it is most likely that the formation of coagulum can be attributed to a lack of stabilisation since no additional emulsifier is added after the shot of TA.

It is well known that small particles could be created by the addition of anionic surfactant, monomer and initiator. However, additional stabilisation must apparently be provided to stabilise the increased particle surface area generated by the new population. Thus, in runs E3.9, E3.10 and E3.13 the amount of surfactant added to the initial latex was increased using a continuous addition of TN. TA was avoided here since it was thought that it would be ‘too efficient’, and lead to a significant renucleation of more particles than were desirable.

3.1.3. E3.9, E3.10 and E3.13

These runs were carried out using Procedure no 3. The parameters that were changed were the amount of surfactant added, the radical flux and the monomer flow rate. Table 5 presents the detailed experimental procedure for each run, and Table 6 the characteristics of the latexes before and after the renucleation period.

As indicated in Table 6, run E3.9 led to the formation of coagulum (coagulum refers to the creation of large lumps of polymer, whereas paste means that the latex did not show any visible lump formation, but the viscosity increased tremendously). Since the last measurable overall conversion accurately determined was very low (<40%), the radical flux was increased in run E3.10 by increasing the concentration of AscA with respect to the amount of monomer added. The final PSD of E3.10 determined by SLS is presented in Fig. 5. The PSD is composed of 93% (v/v) of large particles (950 nm) and 7% of small particles (300 nm).

Table 6
Characteristics of the latexes at the beginning and the end of the renucleation period

Run	Beginning of the renucleation			End of the renucleation stage		
	PC _i (%)	d _p (nm)	I _p	PC _F (%)	d _p (nm)	I _p
E3.9	52	569	0.09	coagulum	-	-
E3.10	53	569	0.09	62.1	Figure 5	
E3.13	59	547	0.09	paste	-	-

Table 7
Detailed experimental procedure for run E3.14

Run	First population	Renucleation surfactant system		θ_i theoretical (%)	AscA addition (g)	Additional TN (g/h)	Addition of monomer (g/h)
		Global amount	Composition				
E3.14	E2.317	1.12 g	34 wt% TA 66 wt% TN	81	0.13	1.12	21

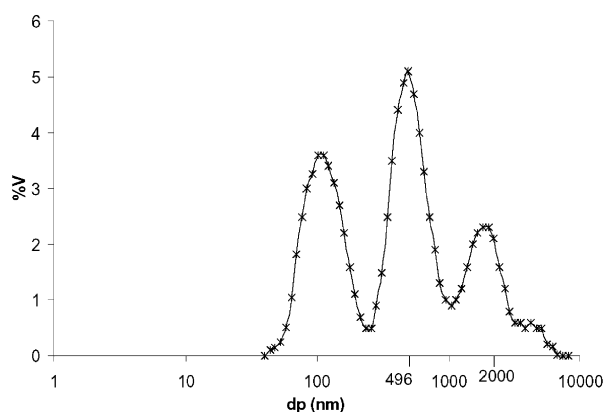


Fig. 6. PSD determined by SLS for the diluted paste obtained in experiment E3.14.

This result allows us to better understand the phenomena involved in the nucleation of the second population. It seems that the radical flux was not high enough for the run E3.9, and the resulting accumulation of monomer provoked the destabilisation of the system. Increasing the radical flux helped to renucleate new particles. However, since only a small amount of surfactant was used, additional stabilisation seems necessary to help create more small particles.

In order to do so, the amount of anionic surfactant, the flow rates of monomer and of TN were all increased in run E3.13. In so far as the radical flux is concerned we chose an intermediate value between E3.9 and E3.10 in order to avoid monomer accumulation and to favour latex concentration by limiting the amount of reactants added. While the system did not totally flocculate, the latex obtained was so viscous that it formed a paste and samples could not be withdrawn to follow the reaction. The very high viscosity observed can be attributed to one of the two things. If no new particles were stabilised, the existing particles grew and the PSD remains monomodal. At solid contents above 50–55%, the viscosity increases sharply as the amount of polymer increases. It is also possible (and more likely) that an excess of small particles were formed. In this case the PSD would be

unfavourable, and the high surface area developed by the small particles led to particle interactions and provoked a sharp increase in the viscosity. Given that renucleation was observed for run E3.10, it is most probable that renucleation also occurred in E3.13. Indeed, the concentration of surfactant was higher for E3.13 than for the previous run, so if renucleation occurred for E3.10, logically it should have occurred for E3.13. It is true that the radical flux was not the same for these runs, but given that the radicals are uncharged this should not change the stabilisation of the latexes and therefore the PSD [1,3]. It was therefore assumed that the renucleation was too extensive in this case and we attempted to decrease the number of renucleated particles by reducing the total amount of surfactant added for the renucleation (θ_i lower), and by reducing the fraction of TA in the emulsifier used to do the renucleation.

3.1.4. E3.14

E3.14 was carried out according to Procedure no 4, and the renucleation was done directly after the synthesis of the first population, and the renucleation surfactant system was composed of both anionic and non-ionic emulsifiers (Table 7). The results of the characterisation of the latex before and after renucleation in run E3.14 are shown in Table 8.

Here again, the latex synthesised was so viscous that it formed a paste and no samples could be withdrawn. However, in order to better understand what occurred during the formation of such latexes we decided to dilute the paste and characterise it by SLS (which was made available by Crayvalley CRO, Creil, France). The PSD from this experiment is presented in Fig. 6.

It appears that renucleation occurred and that some of the renucleated particles were indeed stabilised. Moreover, compared to Fig. 5 (PSD of E3.10) it appears that the size of small particles is much lower and the volume fraction of the small population is much higher. This PSD also explains the very high viscosity observed. Indeed, the very high surface area developed by the highly numerous small particles

Table 8
Characteristics of the latex before and after the renucleation stage

Run	Beginning of the renucleation			End of the renucleation stage		
	PC _i (%)	d_p (nm)	I_p	PC _F (%)	d_p (nm)	I_p
E3.14	60	455	0.17	–	–	–

Table 9
Detailed experimental procedure for runs E3.15 and E3.30

Run	First population	PC _i (%)	θ_i theoretical (%)	$\theta_{P30\%}$ (%)	wt% TA	Flow rate of TN (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.15 (CP)	E2.318	59	82	80	1.28	0.8	0.16	20
E3.30	E2.328	58	96	94	1.40	1.6	0.26	40

favours the interactions between particles, which makes the viscosity increase sharply.

This result is in agreement with the interpretation of the results of run E3.13. In addition there is a very broad peak of particles formed between 1000 and 8000 nm. These particles must be the consequence of a limited flocculation of some of the large particles from the first population with themselves. Indeed, the appearance of the small particles can provoke a redistribution of the surfactant in the reactor, and cause a reduction in the coverage of the particles that is counterbalanced by the auto-flocculation of some particles in order to reduce the global particle surface area (i.e. the surface energy). This redistribution of the surfactant could have involved the formation of scrap but this did not occur since the amount of TN added was sufficient to avoid it.

From this series of experiments where attempts were made to provoke the in situ renucleation of a second population initiated by the redox system H₂O₂/AsCA it was observed that renucleation can occur, but it is difficult to find the right levels of stabilisation needed to control the PSD. It is clear that homogeneous nucleation occurs, but it also not possible to exclude the possibility that micellar nucleation also happens here. In fact we can assume that both mechanisms coexist, as has been shown in the literature [8]. Also, different parameters have to be well adjusted in order to control the renucleation. First, the amount and the composition of the surfactant system added for the renucleation must allow us to create an adequate second population. Also, additional stabilisation must be provided thanks to a sufficient flow rate of surfactant in order to preserve the newly created particles from limited flocculation. If the number of small particles so created is too large the viscosity increases sharply and we obtain a paste. We know that anionic surfactant is required in order to promote the nucleation, but if we want to avoid a massive and uncontrolled renucleation, it must be added in conjunction with the non-ionic surfactant. Indeed, by doing so we decrease the fraction of anionic surfactant while we maintain a sufficient level of stabilisation. It was also observed that the monomer flow rate has to be high enough

to promote the nucleation of new particles, and the flux of radicals has to be adapted to avoid monomer accumulation, which leads to the formation of scrap. Indeed, as shown in the literature [9], the creation of new particles requires a certain concentration of oligomers in the aqueous phase called supersaturation, which corresponds to the ratio of the concentration of oligomers to their water solubility. Finally, we did not succeed in controlling the PSD of the latex with this system where the stabilisation is exclusively provided by the emulsifiers.

It appears that it might be more useful to look for an additional means of fine-tuning the PSD. In fact, in this part of the process the objective is the opposite of that in the previous chapter: we want to favour the stabilisation of the small particles. It is known that charged radicals created by the decomposition of an initiator such as ammonium persulphate (APS) could be used to stabilise particles, even without surfactant. So, to enhance the stabilisation of the newly created particles the use of APS as initiator could be useful.

3.2. Initiation by APS

In this part of the study, the experimental procedure is the same for all the experiments. A solution of mixed surfactant is added to the first population. The use of TA alone leads to loss of control over PSD, and very often to loss of stability, and the use of TN alone is unfavourable for the nucleation of new particles, but it is thought that a judicious combination of the two will help to create and stabilise a controlled number of particles. The solution of surfactant used to this end is typically composed of 30% (w/w) of anionic surfactant and 70% of non-ionic surfactant. The aim is here to increase slightly the fraction of anionic surfactant in the aqueous phase in order to promote a gentle renucleation (i.e. controlled process that does not provoke a massive redistribution as surfactant in the system, and thus destabilise the latex). Boutti et al. [7] showed that for a polymer content of 15%, a large portion of the TA will remain available in the aqueous phase in a mixed surfactant

Table 10
Main final characteristics of the latexes from runs E3.15 and E3.30

Run	PC (%)	η (mPa.s) at 20 s ⁻¹	Large population		Small population	
			d_p (nm)	%V	d_p (nm)	%V
E3.15 (CP)	71.9	984	1110	88	244	12
E3.30	74.1	1581	1140	86	192	14

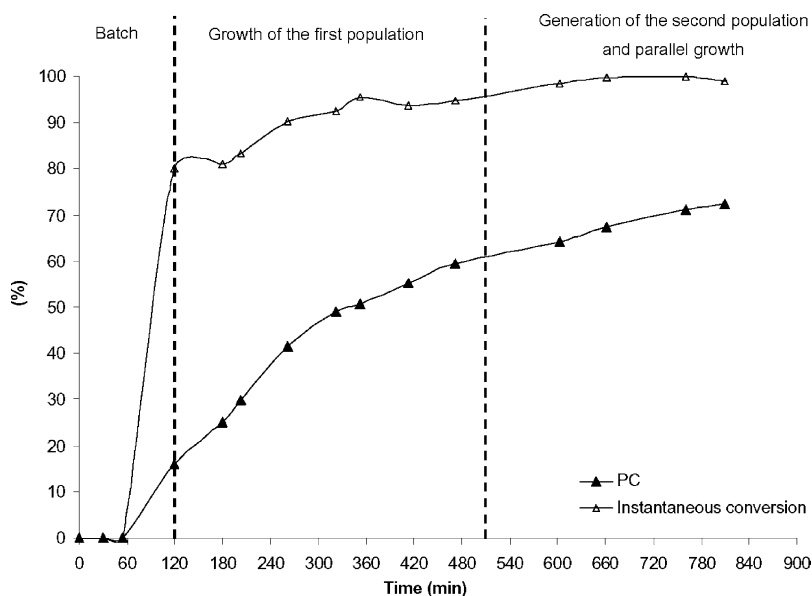


Fig. 7. Instantaneous conversion and polymer content plotted as a function of the reaction time for the entire process for run E3.15.

system. An understanding of how the non-ionic surfactant partitions in such a system would be extremely useful, unfortunately, this was not possible because of technical and time limitations. Therefore, we cannot exclude the possibility that a fraction of TN, and thus a mixed surfactant system, is also present in the aqueous phase.

In this series of experiments, monomer, non-ionic surfactant and initiator are continuously added in three separate streams. Table 9 indicates the experimental procedure for these experiments. As in Section 3.1.4 the name of the first population refers to runs presented in Part I [1]. θ_i theoretical indicates the maximum theoretical surface coverage after the addition of the additional surfactant (assuming no partitioning and exact knowledge of the PSD), and wt% TA corresponds to the weight percent of anionic surfactant with respect to the total amount of surfactant present. The flow rates of TN and monomer are indicated for

100 g of polymer in the first population, but the amount of APS is indicated for 100 g of added monomer.

The main characteristics of the final latexes are shown in Table 10. Here, the final polymer content was determined by gravimetry (PC), the viscosity (RFS III Rheometer from Rheometrics) and the PSD provided by Coulter LS230. In order to compare the PSD of the different runs, we always measured the small and large populations in the same way. In certain cases it is necessary to make an arbitrary choice of the boundaries for these populations: particles between 40 and 400 nm are said to form the small population, and those between 400 and 1500 nm formed the larger one. If there were any particles larger than 1500 nm, they were taken separately. It is important to note that the information provided by SLS is not infallible, but since all the runs are analysed in the same way, the PSD thus obtained are at least comparable. In the nomenclature of the experiments, when the name of the run is followed by Complete Process (CP) it means that the renucleation was carried out directly after the synthesis of the first population. Most of the time the first population was stored overnight in the reactor before the renucleation stage, however, for run E3.17 the entire process was carried out in one single run.

The PSD and viscosity will obviously evolve throughout the whole process. As explained previously, this type of process consists of four main steps (see Fig. 1). It is, however, possible to combine steps three and four, where the processes of renucleation and parallel growth of both populations are concurrent. Fig. 7 shows the evolution of the conversion and the polymer content as a function of the stage of the procedure, and Fig. 8 presents the evolution of the PSD for run E3.15. The recipe of E3.15 corresponds to a complete process where the renucleation was carried out directly after the synthesis of the first population. For a ‘typical’ procedure we add a mixed surfactant solution

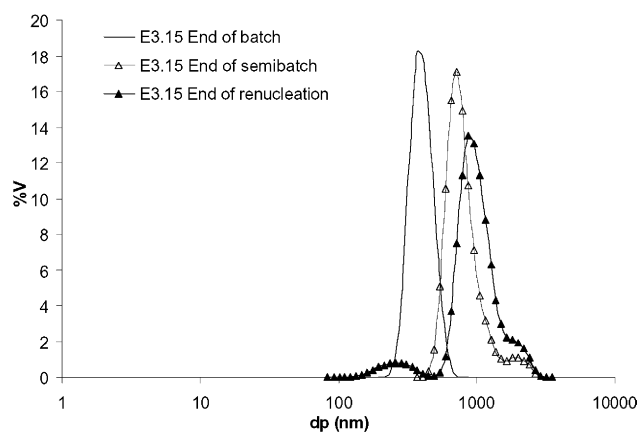


Fig. 8. Evolution of the PSD as a function of the stage of the process for run E3.15.

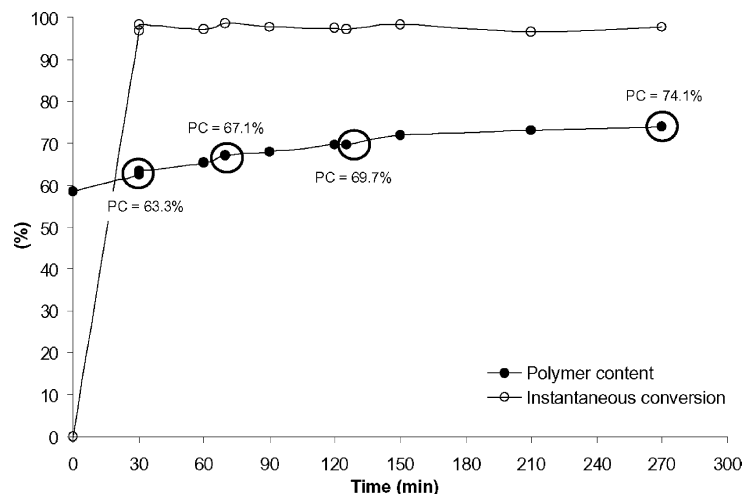


Fig. 9. Evolution of the polymer content and the instantaneous conversion during the renucleation stage for the run E3.30.

(30 wt% TA and 70 wt% TN) to the first population, which makes θ_i theoretical increase to around 85–95%.

Fig. 9 presents the evolution of the polymer content and the instantaneous conversion during the renucleation stage for another typical run, E3.30. Then, Fig. 10 presents the evolution of the PSD during the renucleation stage and the corresponding viscosity for E3.30.

As seen above previously, a significant part of the

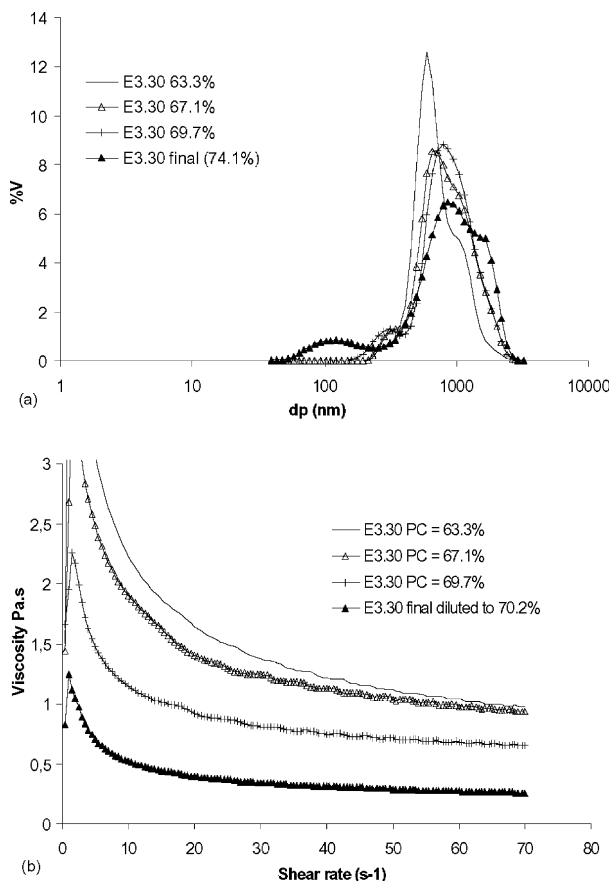


Fig. 10. Impact of the PSD on the viscosity during the renucleation stage.

anionic surfactant added remains available in the aqueous phase. If we consider that 70% of TA remains in water [7] the concentration of anionic surfactant represents $0.96 \cdot \text{CMC}_{\text{TA}}$ for E3.15 and $0.91 \cdot \text{CMC}_{\text{TA}}$ for E3.30. Moreover, we cannot exclude the possibility that a fraction of the non-ionic emulsifier is also available in the aqueous phase and that we are in the presence of mixed surfactant system. In this case of mixed surfactants the CMC is lower than that of TA alone, which makes the presence of mixed micelles possible. Also, if we consider that only 30% of the added anionic surfactant is on the particle surface the surface coverage is closer to $\theta_{\text{P}30\%}$ but even in this calculation θ is overestimated since we still consider that all the TN is on the particle surface.

Fig. 8 shows that the PSD at each step of the process corresponds to the previously defined criteria. Indeed, at the end of the batch, the polymer content is about 20 wt% and the PSD is monomodal and narrow. At the end of the semi-batch step corresponding to the growth of the first population, the polymer content is about 60 wt%. Here, the PSD is composed of large particles with a shoulder of even larger particles. Finally, at the end of the process the polymer content is about 72 wt%, and we obtain a bimodal PSD. Both of the populations are broadly distributed. We observe a shoulder near the very large sizes for the PSD of the initial population. This is due to the limited flocculation of smaller particles in order to reduce the particle surface area. For the small population, the distribution is simply wide. This is due to the fact that we carry out a gentle renucleation, so the renucleation stage is long, and the particles nucleated early are already growing when other particles are still nucleating. This kind of PSD, where the populations are broadly distributed, allows us to obtain a very low viscosity ($\eta = 984 \text{ mPa s}$ at 20 s^{-1}) for a very high polymer content ($\text{PC} = 72\%$).

Fig. 9 presents the evolution of the polymer content and the conversion for run E3.30 during the renucleation stage. If we compare Fig. 9 to Fig. 7 we observe that the increase in

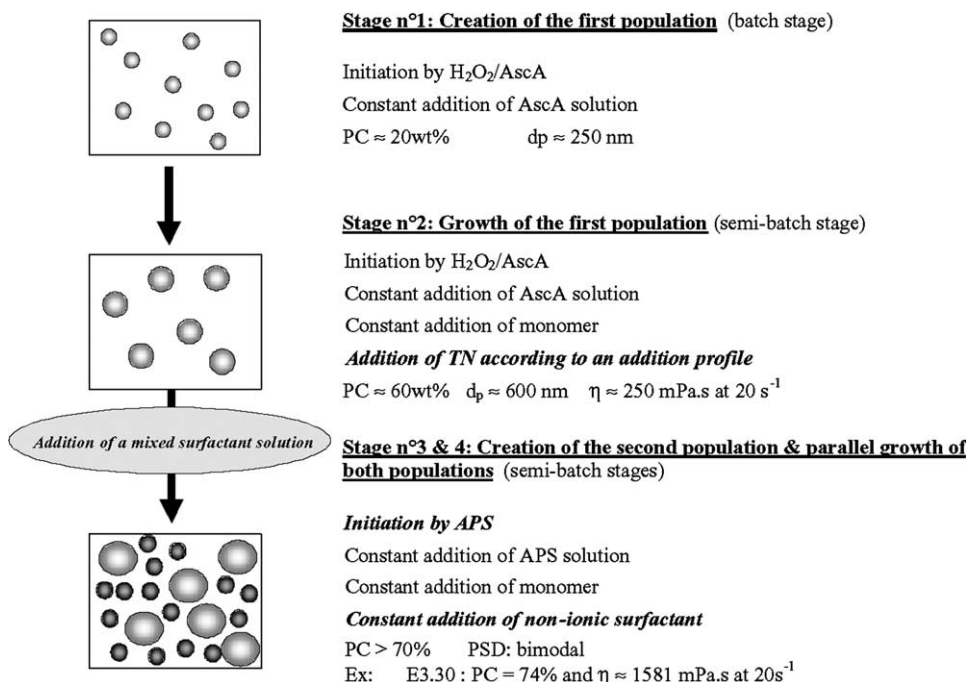


Fig. 11. Diagram of the complete process for the production of HSC/LV latices with no intermediate seeds.

the monomer flow rate and the radical flux allowed us to increase the polymerisation rate since we reach 74.1% polymer content in 270 min for E3.30 while we need 300 min to reach 71.9% for E3.15. The PSD and the corresponding viscosity curves of the points surrounded in the figure above are represented in Fig. 10.

Fig. 10(a) shows the evolution of the PSD during the renucleation stage only for run E3.30. We can observe particles with a ‘medium’ size that disappear into the large population peak while new and smaller particles emerge at the end. The large population continues to grow as the reaction advances. It should be pointed out that this growth is in fact somewhat faster than one could expect from polymerisation alone, so part of it must be attributed to the coalescence of smaller particles onto the larger one. These observations are in agreement with the hypothesis that in order to maintain the new particles at an acceptable size, the last stage of the process has to be relatively short. However, if we want to create new particles quickly, it will not be a gentle renucleation and the danger is to provoke the destabilisation of the entire system. A solution is to continuously create new particles. Indeed, in this way the system is not destabilised, and a significant fraction of small particles is present in the latex at the end of the process.

As we can see in Fig. 10(b), the viscosity of the latex decreases as the fraction of stabilised small particles increases, even though the polymer content increases. This clearly illustrates the impact of the bimodality (multimodality if one wishes to consider the shoulders as separate peaks) on the viscosity of the colloidal dispersions.

4. Conclusion

The objective fixed at the beginning of this series of papers was to synthesise a HSC/LV latex by an unseeded process. The criteria for the final latex were a polymer content $\text{PC} \geq 70\%$ and a viscosity $\eta \leq 1500 \text{ Pa s}$ at 20 s^{-1} , and this has been met with the process using APS and a mixed surfactant system to gently create the second population of small particles.

The final process (combining the results of Parts I and II) is summarised in the Schema in Fig. 11. It consists of the four stages mentioned previously: creation of the first population, the concentration of this population, the generation of the second population and the subsequent parallel growth of the bimodal latex particles. The first two stages are carried out using an electrically neutral initiation system and a time-varying profile of addition of TN in order to avoid the stabilisation of homogeneously nucleated particles.

It turns out that it was not possible to create an adequate second population using the redox system $\text{H}_2\text{O}_2/\text{AscA}$ as initiator. For some runs the newly nucleated particles were not stabilised, and for other runs the small particles were so numerous that we lost control over the PSD and either suffered total coagulation of the latex, or the viscosity increased to such a point that samples could no longer be withdrawn from the latex. In this case, the stabilisation is exclusively due to the surfactants and it appears that reproducible control of the PSD is very difficult. For this reason, we chose to promote the process of homogeneous nucleation using APS as the initiator, coupled with a mixed surfactant system.

The injection of a solution of a mixed surfactant, consisting mainly composed of TN with only traces of TA followed by the continuous addition of TN allows us to generate and stabilise an adequate second population of particles. The moderate initial concentration of surfactant ($\theta_{i \text{ theoretical}} < 100\%$), especially the low fraction of TA, allows us to carry out the renucleation stage gently and reproducibly, in a manner that does not destabilise the system.

Moreover, the process that we developed appears to be reproducible not only in terms of the final PSD and the viscosity, but also for the kinetics. This reproducibility can be attributed to the fact that the renucleation occurs ‘gently’. Indeed, the concept is to make just enough TA available in the aqueous phase to promote a slight renucleation. Then, we add continuously non-ionic surfactant to stabilise these new particles. Also, the use of APS as initiator allows us to promote the stabilisation of the renucleated particles. Thus, at the end of the process we are able to stabilise HSC latexes with a weight fraction of surfactant of about 3% with respect to the amount of polymer. The gentle renucleation procedure implies that the renucleation stage is spread out over a long time, which explains why the small particles are relatively large (~ 250 nm), and why the PSD of the small population is fairly broad.

The sensitivity of the process, and the role of the different components in determining the final PSD will be examined in Part III of this series of papers [10].

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