Control of particle size distribution for the synthesis of small particle size high solids content latexes

Inês de F.A. Mariz, José C. de la Cal, Jose R. Leiza*

Institute for Polymer Materials, POLYMAT and Grupo de Ingeniería Química, Dpto. de Química Aplicada, Facultad de Ciencias Químicas, University of the Basque Country, Joxe Mari Korta zentroa, Tolosa Etorbidea 72, 20018 Donostia-San Sebastián, Spain

ABSTRACT

A polymerization process to synthesize bimodal latexes with maximum particle diameters below 350 nm and solids content above 65 wt% has been developed.

The process is based on an iterative strategy to determine the optimal particle size distribution that gives the maximum packing factor for a given range of particle sizes and at a given solids content. The calculated optimal bimodal PSD was experimentally obtained in a seeded semi-continuous emulsion polymerization reaction as follows: in the first step, a polymer seed latex was loaded in the reactor and grown, under monomer starved conditions, until a given particle size. At this point a fraction of the same seed was added to the reactor and the feed was continued until the desired particle size distribution and solids content were achieved. The point at which the seed was added again to the reactor and the amount of seed required were determined by the iterative strategy and depended on the competitive growth rate ratio of large and small particles that is an input for the iterative strategy.

Implementation of the solution obtained from the iterative strategy, and for the first time in the open literature, led to the production of a coagulum free and stable bimodal latex with 70 wt% of solids content and particle sizes below 350 nm.

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1. Introduction

Latexes are very versatile materials extensively used as adhesives, coatings, textiles, paper paints, floor polish and makeup, in which high solids content (HSC) brings many advantages like maximizing the reactor production, minimizing transportation and storage costs, giving more flexibility in product formulation and improving surface coverage when applied [1–6].

The viscosity of a latex sharply increases with the solids content [7,8], which in turn influences heat removal rate, mixing, mass transfer and stability. The key to obtain high solids content with low viscosities (HSC/LV) is the control of the particle size distribution (PSD). The particles in a perfectly monodisperse latex will enter into contact at solids contents of approximately 64 wt%. This explains why most industrial processes with relatively narrow particle size distribution usually operate at less than 55 wt% of solids content. To overcome this limitation and to accomplish the goals of high solids content and low viscosity the production of bimodal PSD have been considered. In a bimodal PSD, if the

difference on particle sizes is significantly high, small particles will efficiently pack into the voids left by the large particles, thus increasing the maximum packing factor (maximum volume fraction of particles in the dispersion).

However, producing a latex with a target multimodal particle size distribution in a reproducible way is more challenging than producing a monomodal product because reaction times can be long and the stabilization of the particles at different stages during the reaction can be delicate.

Most of the known procedures for the synthesis of high solids content latexes are found in patents. Union Carbide System GmbH [9] achieved bimodal latexes with solids content approximately 65 wt% by a process in which, during the synthesis a part of the latex was withdrawn from the reactor to be re-injected later. The main drawback of this strategy was the storage and extraction of the latex withdrawn from the reactor that contained unreacted monomer. Among companies working on the synthesis of HSC latexes, BASF [10–15] published very interesting works. They described strategies to produce bimodal latexes with solids up to 75 wt% with particles in the range 200 and 1200 nm. Other also interesting patents were published by Rohm and Haas Company [16–18], Atofina [19], Wacker Polymer System GmbH [20], Dow Chemical [21], LG Chem [22] and Tesa AG [23]. A general trend can

be found in all the polymerization procedures presented in these patents. They mentioned directly or indirectly, the importance of producing a latex with broad PSD.

Scientific literature, which is usually more precise and richer in information, only covers a few of the strategies reported in patents. The techniques can be grouped as: physical blends of seeds followed by a step of evaporation of water, miniemulsion polymerizations in batch and semi-continuous process, and semi-continuous emulsion polymerization by seeded or unseeded processes.

Blends of seeds consist in blending monomodal latexes with different particle sizes achieving polydispersed latexes with higher packing. However monomodal latexes will not have higher than 60 wt% of solids and the achievable solids content decreases as the particle size decreases [24]. This means that, a physical blend of seeds will have a final solids content lower than 60 wt% at most. To increase the solids content, a step of evaporation of water is needed. This is not economically advantageous from the industrial point of view. Also, during evaporation the latex stability can be affected leading to flocculation or coagulation. In the works that used this approach [6,25—28] the goal was to study the effect of the ratio of large to small particle sizes and the fraction of each population of particles on the viscosity of the latex. The main conclusions were that large particles must be between 4 and 10 times larger than the small ones and the fraction of small particles must be in the range of 15—20% by volume.

The miniemulsion polymerization process was also mentioned as a possible means to broaden the particle size distribution. Miniemulsions have been used in batch and semi-continuous processes. One of the first academic works using miniemulsion technology was published by Lopez de Arbina and Asua [1]. The authors tried to produce HSC latexes with low viscosity starting from concentrated miniemulsions. They were only able to produce stable latexes with solids contents up to 60 wt%.

Leiza et al. [3] attempted to reduce the amount of surfactant used in the process to produce high solids content latexes by miniemulsion polymerization. Coagulum free latexes with 61 wt% of solids content using less than 1 wt% of surfactant with respect to monomer were produced by seeded semi-continuous emulsion polymerization. The seed was prepared by miniemulsion with the aim of broadening the PSD and hence the final latex PSD.

do Amaral et al. [4,29,30] and Ouzineb et al. [31] also used different miniemulsion polymerization strategies for the synthesis of HSC latexes. do Amaral [4,29,30] explored two strategies to obtain bimodal HSC latexes making use of the miniemulsion polymerization. The most interesting one [30] was a polymerization process that was started with two miniemulsions with different droplet size and was concentrated by semi-continuous miniemulsion polymerization. Using this procedure they were able to obtain bimodal latexes with particle sizes between 200 and 900 nm and solids content around 65 wt%. Ouzineb et al. [31] by using a similar procedure, were able to reach latexes with 70 wt% of polymer content and a viscosity of 650 mPa s at 20 s^{-1}. The final latex obtained had a bimodal PSD with particle sizes ranging from 100 to 900 nm.

Other groups attempted the synthesis of bimodal latexes to produce high solids content latexes by semi-continuous emulsion polymerization. Most of them have in common that the large particle mode had sizes well above 500 nm (typically 800—900 nm) and the small population of particles was created either in-situ during the polymerization taking advantage of the polarity of the monomer to induce secondary nucleations [32] or by injecting shots of anionic surfactant and creating new particles by micellar nucleation [33—38] or by the addition of a seed latex at the intermediate point of the polymerization [39—41]. For instance, Boutti et al. [36,38] prepared latexes with solids content between 65 and 74 wt% with viscosities around 1500 mPa s at 20 s^{-1} and particle sizes in the range 200—1400 nm adding anionic surfactant shots to in-situ create the small population of particles. Schneider et al. [39—41] created a bimodal PSD (particles with 100 and 900 nm) by first growing a seed up to 60 wt% solids and 500 nm. Then they introduced a seed of smaller size (75 nm) and by playing with the type of initiators used (oil-soluble to favor the growth of the large particles) they were able to produce latexes with 73 wt% solids and relatively low viscosities (1000 mPa s at 20 s^{-1}). In all the examples the range of particle sizes was very large (higher than 1 μm). Furthermore, no attempt was done to track or control a target particle size distribution in a reproducible manner. Trial and error procedures were employed to keep the ratio between the large and small particles between 4 and 6, but none of the works controlled the growth of both populations of particles well and hence the PSDs produced were not optimal. The only attempt to control the PSD by other means, than just heuristic knowledge, was proposed by do Amaral et al. [4,42]. The authors proposed a model-assisted methodology that attempted to predict the competitive growth of the small and large particles by means of a polymerization model that was coupled with a viscosity model that predicted the viscosity of the dispersions. The coupled model was claimed to be a screening tool to access reproducible and robust polymerization strategies to synthesize high solids content latexes. As in the works discussed above, Amaral et al. [42] did not consider any constraint on the size of the large particles.

In this work we aimed at the synthesis of high solids content latexes (>65 wt%) with small particle sizes (<350 nm). This is very challenging because, the smaller the particle sizes, the lower the ratio between the large and small particle modes, and hence the lower the maximum packing factor, and the lower the achievable solids content. To achieve this goal, a robust iterative strategy that computes the optimal bimodal PSD based on the competitive particle growth rate was developed. The solution of the iterative strategy also provides other key parameters needed to design a seeded semi-continuous emulsion polymerization to produce the required optimal PSD. Using this iterative strategy, we experimentally demonstrated that a latex with 70 wt% solids with particle sizes smaller than 350 nm could be produced with a PSD closed to the target one.

2. Strategy to synthesize high solids content latexes with low particle size

A polymerization approach to produce HSC latexes in a reproducible manner is presented in Fig. 1. As can be seen the polymerization is carried out in two steps. In the first step a seed with small particle size ($\overline{dp}_{seed}$) and reasonable solids content (sc_{seed}) is added into the reactor. The seed is grown (by the addition of
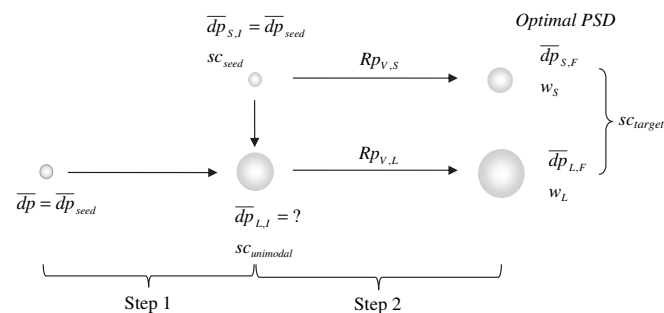

Fig. 1. Polymerization approach to produce a high solids content bimodal latex with the target PSD.

monomer under starved conditions) until a given diameter ($\overline{dp}_{L,I}$) and solids content ($sc_{unimodal}$) lower than the safe limit for unimodal PSD latexes ($sc_{unimodal} << 64$ wt%) is achieved. In the second step, the same seed is added again into the reactor and a bimodal PSD is generated. This bimodal latex is grown by addition of monomer and surfactant (if required) until the target solids content and PSD is achieved.

In order to implement this approach the following information is needed: (1) optimal target PSD defined mainly by $\overline{dp}_{S,F}$, $\overline{dp}_{L,F}$ and w_S (where $\overline{dp}_{S,F}$ and $\overline{dp}_{L,F}$ are the volume average particle size of the small and large particle populations and the weight fraction of the small population of particles required at the end of the polymerization; $w_L = 1 - w_S$); (2) the volumetric growth rate of the small and large population of particles that will grow together in step 2 ($Rp_{V,S}$ and $Rp_{V,L}$); (3) the amount of seed particles (of particle size $\overline{dp}_{seed}$ and solids content sc_{seed}) to be added to the latex grown in step 1, and (4) the optimal time at which the seed particles should be added to the reactor.

The following constraints were considered to gather this information.

The range of the particle sizes must be defined; namely the smallest and largest particle size of the modes of the bimodal PSD. The higher the ratio between the large and small particle populations, the better (the higher is the packing fraction and the lowest the viscosity of the dispersion). In this work the largest particle size was chosen to be 350 nm (this means that the average particle size of the large particles, $\overline{dp}_{L,F}$, must be around 300 nm considering a standard deviation of 10 nm). For the lower end of the PSD the limit was established by the availability of a seed latex with the lowest possible particle size ($\overline{dp}_{seed}$) and highest solids (sc_{seed}) as discussed below.

The solution of the iterative strategy proposed in Scheme 1 provides all the information required to run the polymerization

approach proposed in Fig. 1. First, the target solids content is set, sc_{target}. Then, the average values of the bimodal particle size populations are chosen. In this work as mentioned before, the average value of the largest mode ($\overline{dp}_{L,F}$) was set to 300 nm (to limit the maximum particle size below 350 nm); therefore, the average particle size of the smallest mode, $\overline{dp}_{S,F}$ is assumed. With these average values, the optimal PSD that yields the highest packing fractions is calculated; namely the weight fractions of particles in each mode, w_S and w_L, are determined. With this information, and for a given formulation, the number of particles of each population in the target latex can be calculated. In the next step, and based on the competitive particle growth ratio of both population of particles (see below), it is possible to determine the particle size up to which the initial seed should be grown ($\overline{dp}_{L,I}$). Next step assesses the practical implementation of the approach. Thus, the possibility to achieve the optimal PSD at the given solids content is checked, taking into account the total water content of the latex at the beginning of the competitive particle growth. If the water provided by the small and large population is less than the water content of the final target latex, then the polymerization approach of Fig. 1 is feasible and can be experimentally implemented. If the condition is not fulfilled, we go back to step (ii) and increase $\overline{dp}_{S,F}$ and recalculate all steps until the condition is fulfilled and hence a feasible approach is obtained. Note that it would be possible to obtain a feasible optimal PSD only if the solids content sought is lower than the maximum packing factor calculated. In the following sections each of the steps of the iterative strategy of Scheme 1 are described in further detail.

2.1. Synthesis of the seed latex

One of the requirements of this strategy is the synthesis of a seed latex with small particle size (because it will limit the
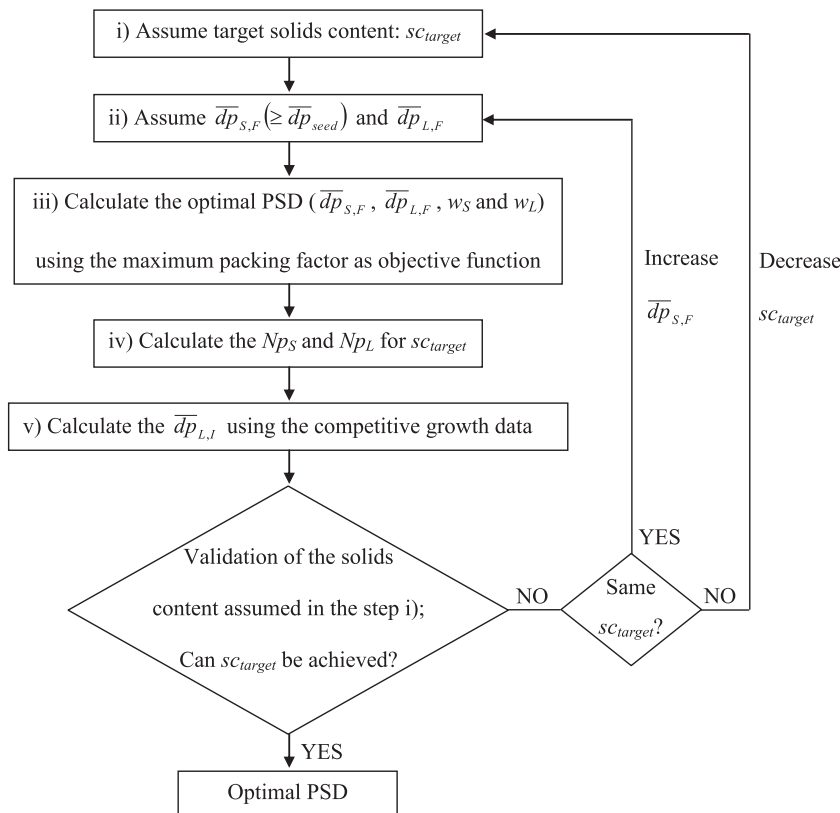
Scheme 1. Iterative procedure to determine the optimal target PSD required to produce a bimodal latex with high solids content and low viscosity.

particle size of the small population of particles) and high solids content (to reduce the dilution effect of the seed when the second population of particles is added again into the reactor). However, producing a latex with small particle size and high solids content is very challenging. A rough idea of the maximum solids content achievable for narrow unimodal latexes can be obtained by considering the interparticle space (IPS) given by the following equation [24]:

$$\text{IPS} = 2r\left(\left(\frac{\varphi_n}{\varphi}\right)^{1/3} - 1\right) \quad (\text{for } \varphi \le \varphi_n \le 0.64) \tag{1}$$

where r is the particle radius, φ_n is the maximum packing factor of the monodisperse particles and φ is the volume fraction of the particles. Fig. 2 plots the interparticle space of narrow unimodal latexes together with a thickness (6 nm) that can be the electrical double layer from an anionic emulsifier or the adsorption layer for a non-ionic emulsifier.

Fig. 2 shows that, the larger the particle diameter, the higher the distance between particles and the higher the solids content that can be reached before the double or adsorption layers of neighboring particles $(2*\delta)$ interact. The straight-line of Fig. 2 was assumed as the safe distance between particles to avoid an excessive increase in the viscosity of the dispersion and/or the risk of coagulation. The cross-points roughly represent the maximum achievable solids content for monodisperse latexes with the given particle sizes.

For achieving the highest packing factor in a bimodal latex, the smaller the particle size of the small population of particles, the better. However, as shown in Fig. 2 ,the smaller the particle size, the lower the achievable safe solids content. For example, for particles of 20 nm, the highest solids achievable should be circa 28 wt%. A seed with low solids content implies a higher dilution of the latex when the second population of particles is added into the

reactor. Consequently, the solids content of the bimodal product cannot be increased without violating the upper limit on particle size (350 nm). This means that a compromise between small particle size and safe high solids content must be reached for the seed. In this work the seed latex used was synthesized following the formulation given by Kohut-Svelko et al. [43] that provided MMA/BA latexes with 50 nm and 40 wt% of solids content, which is within the safety boundary of Fig. 2. Note that any other latex (with smaller or larger particle size) can be used in the iterative strategy presented in Scheme 1.

2.2. Determination of the target PSD

The optimal PSD is the one that gives the maximum packing factor for a given range of particle sizes. The maximum packing factor depends on the diameter, the weight percent and the polydispersity of each population of particles (it is desirable to have narrow distribution of particles in the small and large modes of the bimodal distribution). The higher the difference between particle sizes the higher is the packing; this explains why most of the works reported in the literature synthesize bimodal PSD with diameters in the large mode around 1 μm. The weight percent of small particles that gives the maximum packing factor depends on the diameters and width of each population.

The maximum packing factor (ϕ_n) of a latex with a given particle size distribution, PSD, can be computed by several methods. In this work Ouchiyama's equation [44] was used:

$$\varphi_n = \frac{\displaystyle\int_0^{\infty} dp^3 n(dp)\partial(dp)}{\displaystyle\int_0^{\infty} |dp \succ \overline{dp}|^3 n(dp)\partial(dp) + \frac{1}{\beta}\int_0^{\infty}\left[(dp + \overline{dp})^3 - |dp \succ \overline{dp}|^3\right]n(dp)\partial(dp)} \tag{2}$$

Where

$$\beta = 1$$

$$+ \frac{4}{13}\left(7 - 8\phi_m^0\right)\overline{dp}\frac{\displaystyle\int_0^{\infty}(dp + \overline{dp})^2\left(1 - \frac{3}{8}\frac{\overline{dp}}{dp + \overline{dp}}\right)n(dp)\partial(dp)}{\displaystyle\int_0^{\infty}\left(dp^3 - |dp \succ \overline{dp}|^3\right)n(dp)\partial(dp)} \tag{3}$$

and $n(dp)$ is the number density distribution, dp is particle diameter, $\overline{dp}$ is the number average particle diameter and ϕ_m^0 is the porosity of a monodisperse system. In this work, ϕ_m^0 was taken from Lee [45] ($\phi_m^0 = 0.361$).

To obtain the bimodal PSD that yields the maximum packing factor an optimization was solved. The bimodal number PSD was built as the sum of two Gaussian distributions characterized by the average particle sizes ($\overline{dp}_{S,F}$ and $\overline{dp}_{L,F}$) and the standard deviation of the each mode (SD_S and SD_L) as follows:
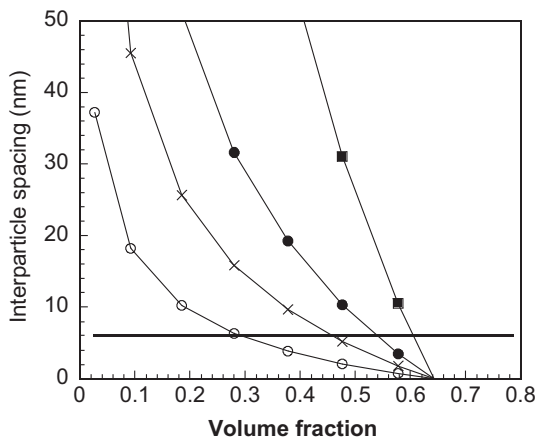
Fig. 2. Interparticle spacing *vs.* volume fraction of particles as a function of particle diameter. *Legend:* The horizontal line represents the safe interparticle distance (○) particle diameter of 20 nm (×) particle diameter of 50 nm (●) particle diameter of 100 nm (■) particle diameter of 300 nm.

$$n(dp) = \frac{1}{\sqrt{2\pi}(SD_S)}\exp\left[-\frac{\left(dp - \overline{dp}_{S,F}\right)^2}{2(SD_S)^2}\right]n_S$$

$$+ \frac{1}{\sqrt{2\pi}(SD_L)}\exp\left[-\frac{\left(dp - \overline{dp}_{L,F}\right)^2}{2(SD_L)^2}\right](1 - n_S) \tag{4}$$

where n_S is the number fraction of small particles.

The goal of the optimization was to determine the number fraction of small particles that makes φ_n maximum for a given average particle size of the small and large populations and standard deviations of each mode, provided that the entire PSD was in the range 50–350 nm. Note that this limit was imposed because as discussed above, latexes with smaller particle sizes yield better films and hence better application properties. The optimization was solved by the Nelder–Mead algorithm [46] using the DBCPOL subroutine from the IMSL library.

2.3. Calculation of the number of particles of each population for the target solids content

For a given target solids content, sc_{target}, and the optimal PSD calculated above (defined by the average particle sizes of each mode, $\overline{dp}_{S,F}$ and $\overline{dp}_{L,F}$, and the weight percentage of each mode, w_S and w_L), the total number of particles in each population can be readily calculated as follows:

$$Np_S = \frac{6 w_S sc_{target} Y}{\pi \rho_{pol} \overline{dp}_{S,F}^3} \tag{5}$$

$$Np_L = \frac{6(1 - w_S) sc_{target} Y}{\pi \rho_{pol} \overline{dp}_{L,F}^3} \tag{6}$$

where Y is the total mass of the formulation and ρ_{pol} is the density of the polymer.

Thus, the amount of particles of the small seed required in the initial charge should be Np_L and the amount of the seed particles to be added when the initial charge will reach the size $dp_{L,I}$ should be equal to Np_S. Obviously, this implies that during the second step (growth of both small and large particles) secondary nucleation or coagulation must be avoided by proper feeding of monomers and surfactant.

2.4. Calculation of the $\overline{dp}_{L,I}$ based on competitive particle growth data

The key point for a successful implementation of the solution of the iterative strategy is the knowledge of the competitive particle growth of the bimodal latex. This knowledge will allow the control of the PSD and hence the robust and reproducible synthesis of a latex with high solids content. The more accurate is the prediction of the ratio of the volumetric growth of both large and small particle populations, the better the control of the target particle size distribution. This feature has been ignored in most of the works reported in the literature that aimed at producing high solids content latexes by means of creating bimodal PSDs.

In this work a simplified approach was used to determine the competitive growth ratio of large to small particles. A single experiment was made to determine the volumetric growth rates of small and large particles polymerizing simultaneously at relatively high solids content. Further details of the experiment are given below in the experimental section. The ratio of the volumetric growth rates ($k = Rp_{V,L}/Rp_{V,S}$, where $Rp_{V,L}$ and $Rp_{V,S}$ are the volumetric particle growth rates (cm^3/s) for the large and small particles, respectively) was then used in the iterative strategy to determine $\overline{dp}_{L,I}$, namely the particle size up to which the initial seed particles must be grown. $\overline{dp}_{L,I}$ was calculated as follows:

$$Rp_{V,L} = k Rp_{V,S} \tag{7}$$

$$\overline{dp}_{L,F}^3 - \overline{dp}_{L,I}^3 = k\left(\overline{dp}_{S,F}^3 - \overline{dp}_{S,I}^3\right) \tag{8}$$

$$\overline{dp}_{L,I} = \sqrt[3]{\overline{dp}_{L,F}^3 - k\left(\overline{dp}_{S,F}^3 - \overline{dp}_{S,I}^3\right)} \tag{9}$$

Once $dp_{L,I}$ is known, one can calculate the time needed to grow the seed particles ($\overline{dp}_{seed}$) to this size, provided that secondary nucleations do not take place during the polymerization and that the feeding rate of the monomer is known (which is a process variable defined by the user).

2.5. Validation of the target solids content assumed in the iterative strategy

To assess if the calculated optimal PSD at the target solids content can be produced experimentally it is necessary to check if the amount of water added with the small seed shot before starting the second step, and the amount of water required to have a latex with the safe solids content, $sc_{unimodal}$, and the particle size calculated by the competitive growth data, $\overline{dp}_{L,I}$, is lower than the amount of water of the latex sought. To check this point the amount of water added with the seed particles at the beginning of step 2 ($Vwater_S$) is first calculated:

$$Vwater_S = \left(\frac{1}{sc_{seed}} - 1\right)\frac{\pi}{6}\rho_{pol} Np_S \overline{dp}_{S,I}^3 \tag{10}$$

Then, the amount of water of the initial seed grown until a size $\overline{dp}_{L,I}$ and with a solids content $sc_{unimodal}$ ($Vwater_L$) is calculated:

$$Vwater_L = \left(\frac{1}{sc_{unimodal}} - 1\right)\frac{\pi}{6}\rho_{pol} Np_L \overline{dp}_{S,L,I}^3 \tag{11}$$

If $Vwater_S + Vwater_L \leq Y(1 - sc_{target})$ the solution of the iterative strategy is feasible and can be applied experimentally.

3. Experimental section

3.1. Materials

Methyl methacrylate and butyl acrylate (Quimidroga) were used as supplied. Potassium Persulfate (Aldrich) was used as thermal initiator and the couple TBHP/FF7 (Tert-Butyl Hydroperoxide, Aldrich) and (Bruggemann Chemical) was used as redox initiator. NaHCO$_3$, supplied by Riedel-de Haen was used as buffer. Dowfax 2A1 (alkyldiphenyloxide disulfonate, Dow Chemical Co.) and SLS (sodium lauryl sulfate, Sigma–Aldrich) were the anionic surfactants used. Methacrylic acid (Quimidroga) was used as functional monomer. To increase the pH of the latexes a 25% solution of ammonia was used.

3.2. Synthesis of the seed latex

The seed latex was produced batchwise in a 1 L jacketed glass reactor at 40 °C and a stirring speed of 200 rpm. The formulation was taken from Kohut-Svelko et al. [43] and is presented in Table 1.

The monomers, water, surfactant and buffer were added into the reactor. When the reactor reached the desired temperature (40 °C), the redox couple was added as a shot into the reactor vessel. A coagulum free and stable latex was achieved. The volume average size of the latex produced was 49 nm and the solids was 40 wt%. Fig. 3 displays the PSD of the latex measured by CHDF and a TEM micrograph of the particles.

Table 1
Formulation used to prepare the seed latex.

Ingredient	Charge (wt%)
MMA	19.60
BA	19.60
Water	59.15
SLS	1.60
NaHCO$_3$	0.02
TBHP	0.01
FF7	0.02

3.3. Competitive growth experiment

In order to determine an approximate k value (ratio of volumetric particle grow of large to small particles), a seeded semi-continuous experiment was carried out. The experiment consists of growing a blend of two seeds of particles with different particle
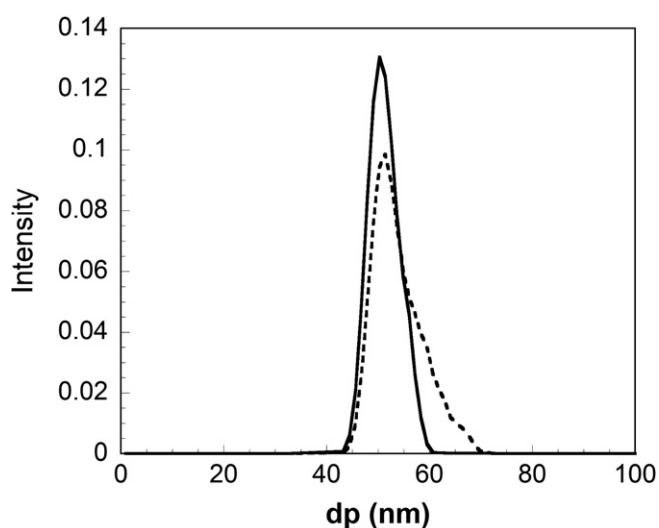

Fig. 3. PSD (solid line by number and dashed line by weight) and TEM micrograph for the seed latex.

sizes by the addition of monomers (MMA, BA and MAA) and surfactant up to solids content of 65 wt%. The initial diameters and weight fraction of small and large particles are given in Table 2.

3.4. Synthesis of bimodal latexes with the target solids content

The polymerization was carried out in 1 L reactor at 75 °C and 200 rpm. The reaction started with the computed amount of seed polymer (Np_L particles of the seed), a small amount of monomers and the water. When the desired temperature was reached, the initiator was added and after a short period (around 5 min) the addition of the monomers, surfactant and ammonia was started at constant feeding rate. After the time needed to grow the initial seed, $\overline{dp}_{seed}$, to the calculated value, $\overline{dp}_{L,I}$, an amount of seed (that is required for adding Np_S particles) was introduced into the reactor shot wise, keeping the feeding of monomers, surfactant and ammonia to reach the desired solids content (sc_{target}). After the feeding period (total of 240 min) the reaction was left to react for 1 h in batch.

3.5. Synthesis of an unimodal latex at 58 wt% solids

With the purpose of comparison, an unimodal latex was synthesized by seeded semi-continuous polymerization using the seed latex described before. The reaction was carried out in a 1 L jacketed glass reactor at 75 °C and 200 rpm. A given amount of the seed latex (note that the amount of seed latex determines the final particle size), water, and a small amount of monomers were added to the reactor. When the temperature inside the reactor reached 75 °C, 0.5 wt% (with respect to the monomers) of the thermal initiator was added as a shot into the reactor. Then a pre-emulsion of the monomers, surfactant (0.8 wt% with respect to the monomers) and water was continuously fed under starved conditions until the desired particle size and solids content was reached.

The volume average particle size of the latex produced was 220 nm and the solids content was 58 wt%.

3.6. Characterization

Solids content and monomer conversion were determined by gravimetry.

Particle size distributions (PSD)s were measured by Capillary Hydrodynamic Fractionation Chromatography (CHDF) (CHDF-2000 from Matec Applied Sciences). The CHDF was operated under the following experimental conditions: flow rate of 1.4 ml/min; temperature of 35 °C; detector wavelength at 200 nm; sample concentration < 0.5 wt% solids; carrier fluid of 1/4X-GR500 (Matec); PSD analysis Matec software v. 2.3. Samples were injected into the instrument and the analysis time was around 15 min.

It was found that the CHDF overestimated in most cases the weight fractions of the populations of large and small particles for MMA/BA/MAA bimodal latexes. The use of custom extinction files in the CHDF analysis software did not improve the results. Consequently, a two step technique (CHDF + ultracentrifugation) was used to characterize the PSD of the bimodal latexes. The weight

Table 2
Volumetric growth rate calculated from the competitive growth experiments at high solids content.

Latex	$\overline{dp}_V$ [a] (nm)	wt%	Rp_V	$Rp_{V,L}/Rp_{V,S}$
Mode 1	49	10.2	1.47×10^{-18}	21.36
Mode 2	228	89.8	3.14×10^{-17}	

[a] Initial volume average particle size calculated for each population from the CHDF.

fraction of small particles was obtained gravimetrically after ultracentrifugation at 35,000 rpm, 4 °C for 15 min. The supernatant was injected in the CHDF and it was found that no large particles were present. A similar procedure was already used in the literature by Chu et al. [47]. The PSDs obtained by CHDF were then normalized and adjusted to the calculated values of weight fraction obtained by the fractionation of the particles.

Transmission electron microscope, TEM, was also used to characterize the PSD. The samples were analyzed by negative staining with a Tecnai™ G² 20 Twin device at 200 kv (FEI Electron Microscopes). Latex samples were diluted (solids content depending on particle size) and stained with 0.5% aqueous solution of phosphotungstic acid. A drop of the stained sample was placed on copper grids covered with formvar (polyvinyl formal, Fluka) and left in the fridge at 3 °C. Micrographs were taken at different magnifications depending on particle size.

The viscosity profile of the latexes was measured at 10 °C with a rheometer TA instruments AR 1500 model. Measurements were carried out by continuous increase of shear rate from 10^{-3} to 10^{5} s^{-1}. A 40 mm flat plate at 50 micron gap was applied.

4. Results and discussion

The polymerization approach described in Fig. 1 was implemented with the solution of the iterative strategy for the production of a bimodal latex of MMA/BA/MAA (49.5/49.5/1) with 70 wt% of solids content. The iterative strategy requires the ratio of the volumetric growth rate of large to small particles, k. This was roughly estimated from a single experiment carried out with seed particles of 49 nm and 228 nm. Fig. 4a presents the time evolution of the volume average particle size of both populations for that experiment.
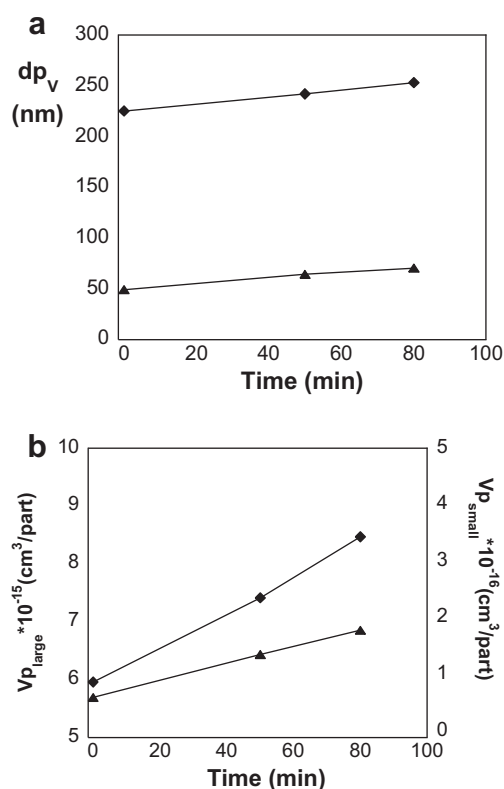
Table 3
Formulation to produce a bimodal latex with 70 wt% solids with the optimal PSD calculated with the strategy of Scheme 1.

Compound	Initial charge (g)	Feed (g)	Shot[a] (g)
Seed	5.06		54.69
MMA	0.4	265.0	
BA	0.4	265.0	
MAA		5.3	
Ammonia		5.3	
Water	204.9		
KPS	2.68		
Surfactant		4.23	

Feeding period: 4 h; cooking time: 60 min; temperature: 75 °C.
[a] Added to the reactor at $t = 141$ min.

The volumetric growth rate ratio, k, was calculated from the slopes of the time evolution of the volume of the particles (Fig. 4b). This ratio depends on the monomer concentration in the polymer particles $[M]_p$, and on the average number of radicals per particle, $\bar{n}$. However, simple calculations of the monomer concentrations by the Morton equation [48] (equilibrium conditions) under very low monomer concentrations (as the starved conditions of the experiments of this work) show that the dependence with the particle size is negligible. Therefore, k is only a function of the ratio of the average number of radicals per particle ($k \propto \bar{n}_L / \bar{n}_S$). If the ratio between the average number of radicals per particle for small and large particles changes along the polymerization, the k value might not be constant. However, Fig. 4b shows that the growth rate of each population is roughly constant in the growing range of this experiment and hence, for simplicity in the implementation of the iterative algorithm, the volumetric growth ratio calculated from the linear fitting of each population growth was assumed constant and the value obtained is displayed in Table 2 ($k = 21.36$).

The solution of the iterative strategy using the k value obtained from the competitive growth experiment and the information of the seed latex ($\overline{dp}_{seed} = 49$ nm and $sc_{seed} = 40$ wt%) was: (i) target PSD with particles of 80 nm ($\overline{dp}_{S,F}$) and 17 wt% (w_S) in the small mode and particles with 300 nm ($\overline{dp}_{L,F}$) and 83 wt% (w_L) in the large mode with standard deviations of 5 and 10 nm for the small and

Fig. 4. Time evolution of the volume average particle sizes (a) and volume of the particles (b) for the small and the large population during the competitive growth experiment. Legend: (♦) large particles (▲) small particles.
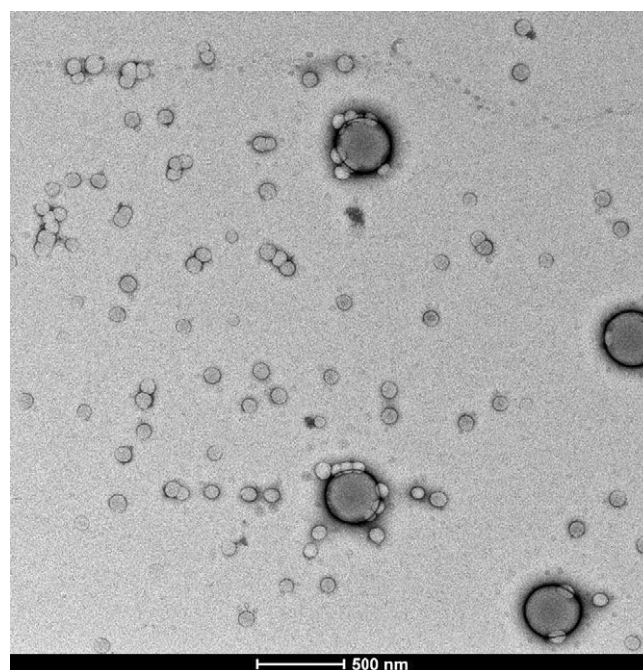

Fig. 5. TEM micrograph at the end of the polymerization for the bimodal latex with 70 wt% of solids content.
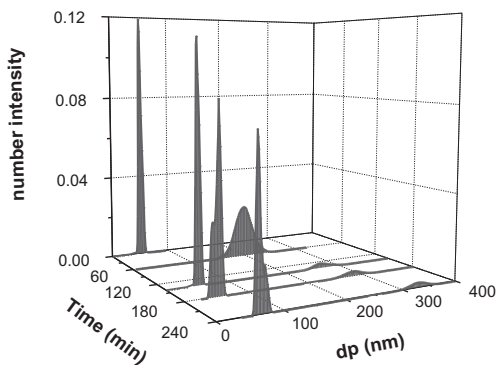
Fig. 6. PSD evolution during the polymerization process for the bimodal experiment.

large modes, respectively; (ii) the diameter at which the first population of particles must be grown was $\overline{dp}_{L,I} = 265$ nm at a safe solids content ($sc_{unimodal}$) of 60 wt% (see Fig. 2); (iii) the amount of seed polymer to be added at $\overline{dp}_{L,I} = 265$ nm was 54.69 g Table 3 presents the formulation used to run the experiment to produce the target optimal PSD and hence produce a latex with 70 wt% solids.

Following this formulation a coagulum free bimodal latex with 70 wt% of solids content and particle size lower than 350 nm was obtained. As can be seen in the TEM micrograph (Fig. 5), two well-defined populations of particles with diameters below 350 nm were obtained.

The evolution of the PSD was followed during the polymerization process and it is presented in Fig. 6.

During the first step (up to 140 min of the polymerization) only one population of particles was present in the reactor, and the particle growth was as expected (from 49 to 265 nm). This was achieved working under starved conditions and surfactant amounts below the cmc. At 141 min, the seed was added and the two populations of particles grew together until the end of the polymerization process (240 min). Fig. 7 shows the comparison between the experimental and target PSD (by weight). The characteristics of the experimental and target PSDs are also presented in Table 4.

As can be seen, the obtained PSD is not exactly the target one; the large particles were bigger (327 nm instead of 300 nm) and the small ones were smaller (60 nm instead of 80 nm). Even though the PSD was not the target one, a coagulum-free and stable latex with 70 wt% solids and particles lower than 350 nm was synthesized. The target PSD was not obtained because a single experiment was used to determine the competitive particle growth. As discussed
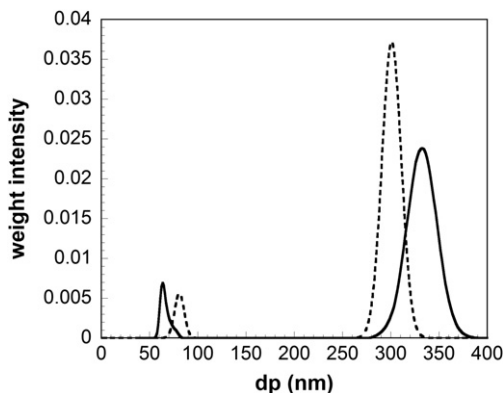
Table 4
Characteristics of the target and experimental PSD.

	Target PSD	Experimental PSD
$\overline{dp}_{L,F}$ (nm)	300	327
$\overline{dp}_{S,F}$ (nm)	80	60
w_S (wt%)	17	7
w_L (wt%)	83	93
φ_n	0.72	0.688[a]
φ_w[b]	0.74	0.712

[a] $\varphi_n = \varphi_{unimodal}/w_L$ because equation (2) can not be applied due to the large fraction of the large particles [43]. $\varphi_{unimodal} = 0.64$.
[b] maximum solids content: $\varphi_w = \varphi_n\rho_{pol}/(\varphi_n\rho_{pol} + (1-\varphi_n)\rho_{aq})$ where ρ_{pol} is the polymer density and ρ_{aq} is the density of the aqueous phase.

above, k depends on the ratio of the particle sizes of the large and small populations (because the ratio of the average number of radicals per particle does so too). Since the ratio of particle sizes used in the competitive growth experiment was different from that used in the optimal bimodal experiment, the growth of the bimodal population of particles was different from that predicted in the iteration algorithm and a deviation occurred between the target and the obtained PSDs. Therefore to correctly track the target PSD, a more accurate value of the competitive particle grow rate ratio, k, is required. This can be obtained either by using the new k value calculated from this experiment or by designing competitive growth experiments in larger ranges of particle sizes and weight ratios. This will allow to correctly determine the variation of k for the growth of bimodal latexes with very different particle sizes. Alternatively, a robust and predictive mathematical model should be developed to predict this key parameter of the proposed strategy. The competitive growth of bimodal latexes at high solids content will be addressed in future publications.

Finally, Fig. 8 plots the viscosity *versus* shear rate for the bimodal latex synthesized with 70 wt% solids and upon dilution to 65 wt% and 58 wt% solids.

These viscosity profiles are compared with those obtained for an unimodal PSD latex at 58 wt% of solids with an average particle size of 220 nm. The viscosity was very high for the latex at 70 wt% solids (because the fraction of small particles was too low). Note that the solids content achieved was quite close to the maximum achievable for the PSD produced (see Table 4) and hence the viscosity was very high. However, as shown in Fig. 8, when the 70 wt% latex was diluted to 65 wt% and 58 wt% solids, the viscosity was significantly lower than that of the unimodal latex with 220 nm at 58 wt% solids in the whole shear rate range. This result strengthens the importance of the production of bimodal PSDs latexes.
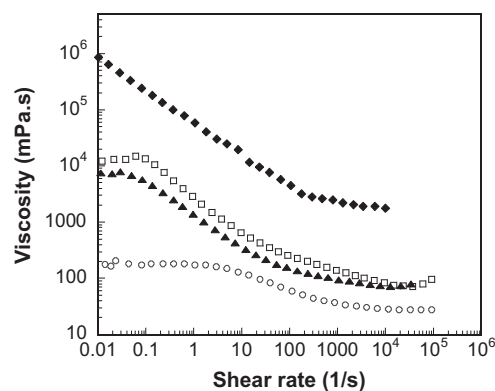

Fig. 7. Experimental and target PSD (by weight) at the end of the polymerization process. *Legend:* (——) experimental (⋯) target.

Fig. 8. Comparison between the viscosity profile for a bimodal latex at high solids content with particles smaller than 350 nm and an unimodal latex at 58 wt% solids and $\overline{dp}$ of 220 nm. *Legend:* (◆) bimodal PSD at 70 wt% of solids (▲) bimodal PSD at 65 wt% solids (○) bimodal PSD at 58 wt% of solids (□) unimodal latex at 58 wt% of solids.

5. Conclusions

A polymerization approach to synthesize latexes with high solids content and a target bimodal PSD was developed. The polymerization was carried out in two steps. In the first step a fraction of a seed of small particle size and reasonable solids content was added in the reactor and grown by the addition of monomers and surfactant up to desired diameter and solids content. At this point a bimodal PSD was created by adding a fraction of the same seed into the reactor. The bimodal latex was then grown until the desired PSD is produced at the solids content required.

This polymerization approach requires the determination of the optimal PSD for a given range of particle sizes. This can be obtained by an iterative strategy subject to some constraints including the particle size range and solids content of the seed latex available. The knowledge of the volumetric particle growth rate ratio of bimodal latexes is the key point of the iterative strategy.

Applying this strategy it was possible to obtain for the first time in the open literature a coagulum-free and stable bimodal latex with particles lower than 350 nm and solids content of 70 wt%. The PSD of the latex was not the target one because the competitive growth rate ratio of the bimodal latex used was obtained from a single experiment and was not accurate enough. Nevertheless, the latex once diluted at 65 wt% solids presented a viscosity *versus* shear rate profile lower than an unimodal latex of 220 nm at 58 wt% solids.

The use of more accurate k values will allow to produce latexes in this range of particle size (50–350 nm) with solids content of 70 wt% and lower viscosities by means of a fine control of the target PSD obtained from the iterative strategy and the robustness of the proposed polymerization approach. This will be shown in future publications.

Acknowledgments

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