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# **Bimodal high solids content latices using RAFT-mediated polymerization-induced self-assembly and semi-batch emulsion polymerization**

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**Keywords:** high solids content, bimodal distribution, RAFT, emulsion polymerization, viscosity.

## **Abstract**

This work focuses on increasing the solids content of water-based coating materials such as paints, other coatings or adhesives while attempting to reduce the amount of surfactant in the final latex. The synthesis of a latex with a bimodal particle size distribution was carried out by combining RAFT and classical emulsion polymerization processes. By employing the RAFT polymerization, the population of small particles was created by self-ordering the block copolymer chains, consisting of a hydrophilic block based on methacrylic acid or sodium 4-styrenesulfonate and another hydrophobic block based on styrene. The final latex was made by adding a pre-emulsion prepared from the latex of small particles and a mixture of monomers and surfactants to the latex of large particles made via conventional emulsion polymerization. The final bimodal latex thus obtained had a solids content of 65% mass with a viscosity value of around 2.0 Pa.s at a shear rate of 20 s<sup>-1</sup>.

## **1. Introduction**

Emulsion polymerization is an industrially important method for the production of water-based coating materials employing synthetic polymers.<sup>1</sup> These products are used in a variety of

applications, including vinyl and acrylic paints, paper coating, textile fibers, and vinyl adhesives.<sup>2</sup> In most emulsion polymerization processes used in industry, the solid content of the latex, that is, the volume of polymer in relation to the total volume of latex, is between 50 and 55 vol%. However, there is continued interest in producing latex with ever higher solid contents. In addition to increasing space-time yields and reducing water consumption, industry also benefits from reduced costs for transporting the final product, faster drying times and fewer defects in the final product when it is used in the form of a film.<sup>3</sup>

One of the major obstacles to overcome when increasing the solid content is that for reasonably monodispersed products the viscosity can increase sharply above 55 vol%. The increase in viscosity is obviously undesirable for any number of reasons.<sup>2,4</sup> One of the ways to overcome such an obstacle is to make latices with either very broad or bimodal particle size distributions. It has been shown that a bimodal distribution with 80 vol% large particles, and a diameter ratio of 6-8 can lead to a latex with a solid content close to 70 vol% and with low viscosity.<sup>5</sup>

Generally speaking, multimodal latices can be obtained in two different ways: i) by blends of monomodal latices of particles with well-defined diameter followed by a semi-batch polymerization step to reconcentrate the mixture (by definition the monomodal seeds will have a lower solid content than an optimally designed bimodal latex); or ii) by creating a seed in situ, then renucleating, or introducing a second population of small particles in the reactor, once again followed by a concentration step.<sup>2</sup> From a purely commercial point of view, reconcentrating a mixture of particles is time consuming and generally less desirable than the ability to control the particle size distribution (PSD) in situ.

For instance Scheneider et al.<sup>6</sup> synthesized stable bi- and trimodal latices from a mixture of methyl methacrylate, butyl acrylate and acrylic acid by trying to nucleate a second population of particles in the presence of a concentrated seed by introducing enough surfactant to go beyond the CMC. Like Chu et al.<sup>7</sup> observed before them, these authors found they were limited to a viscosity near 2500 mPa·s at 20 s<sup>-1</sup> with this method because of the rapid formation of the small particle population which destabilized the latex. In order to avoid such destabilization, Boutti et al.<sup>8-10</sup> generated the second population in situ, but much more slowly so the rate of appearance of the second population was slow enough that the formation of this second population of particles did not destabilize the bimodal product. They obtained a latex with a solid content of 74 vol% and

a viscosity close to 1581 mPa·s at 20 s<sup>-1</sup> with this method. It is important to underline that in the works by Schneider et al. and Boutti et al., the maximum particle size was on the order of 800-1000 nm for the large particles. This is an important point since it has been shown that it is much more difficult to obtain high polymer contents with small particles than with larger ones because in the former case the volume fraction of the stabilizer relative to polymer is much higher.

Moraes et al.<sup>11</sup> attempted to make high polymer content latices with a maximum size of around 200 nm. This implied that the ideal size of the small population of particles would be close to 30 nm, but this proved very difficult to achieve in situ. Their solution was to create a population of very small (< 80 nm) cross-linked particles incorporated in the pre-emulsion fed to a previously formed population of larger particles. Solid contents of 58 wt.% (≈55 vol%) were obtained, but beyond this limit it was found that the small particles swelled during the concentration stage despite the fact that they were cross-linked, leading to a non-ideal particle size ratio.

Mariz et al.<sup>12</sup> used an iterative strategy to determine the optimal particle size distribution to give the maximum packing factor for a given range of particle sizes synthesized by emulsion polymerization a coagulum-free and stable bimodal latex containing methyl methacrylate/butyl acrylate/methacrylic acid with 70 wt.% of solids content and particles size lower than 350 nm. The bimodal latex was formed in two steps. In the first one, a seed of small particles was added into the reactor, followed by constant feeding rate of monomers, surfactant and ammonia until solids content close to 65 wt.%. In the second step, the seed of small particles was added into the reactor again for generation of the second particles population. The feeding of the reactor continued until the larger particles reached a diameter between 300 and 350 nm.

Dearbina and Asua<sup>13</sup> synthesized and compared the stability of high solids content latices synthesized through miniemulsion and emulsion polymerizations. The solids content was varied from 35 to 75 wt.%. The results showed that the latices obtained by miniemulsion polymerization were more stable than the latices obtained by emulsion polymerization. For the latices formed by miniemulsion polymerization no coagulum was found up to a 60 wt.% solids content. However, the latices from emulsion polymerization coagulated over 50 wt.%. This difference was attributed to the monomer droplet nucleation mechanism occurring in miniemulsion polymerization. When the monomers were pre-emulsified in the presence of surfactant and cosurfactant by ultrasonication, the size of the monomer droplets decreased and the total surface area of the monomer droplets increased and thereby droplet nucleation competed with the conventional

mechanisms of nucleation. It is clear from the previous body of work that the key to attaining high solids with an acceptable viscosity is the ability to inject or create a second population of small particles in a large particle seed in a controlled manner. Simply injecting a separate latex of small particles into a semi-concentrated latex of large ones would simply dilute the bimodal latex and prolong the period necessary to achieve high polymer contents. Rapid nucleation of this second population leads to a rapid redistribution of the surfactant in the latex, and to its subsequent destabilization and coagulation. Therefore, in the current paper we will explore different possibilities of obtaining a bimodal high solid content latex with maximum particle diameters on the order of 200-250 nm for the large population, meaning that the small population should be on the order of 30 to 50 nm. We will compare the approach used by Moraes et al. to the one where the small particles in a bimodal latex are made using polymerization-induced self-assembly (PISA) via reversible addition–fragmentation chain transfer (RAFT) polymerization.<sup>14</sup> PISA, which was initially reported by Ferguson et al.<sup>15</sup> in water with RAFT, relies on the use of solvophilic living macromolecules (such as the ones that can be obtained by RAFT), which are chain-extended by a solvophobic block, leading to the self-assembly of the as-formed block copolymers. The further growth of the solvophobic block can then resume into the resulting block copolymer particles that are generally small (< 100 nm). The process has focused a lot of attention recently, and can be performed either in dispersion polymerization or under aqueous emulsion conditions, which will be the case in the present study. The advantage of PISA is that we can control the size of the particles that are self-stabilized and do not involve any molecular surfactant usually necessary to make particles on the order of 30 to 40 nm. In addition, the stabilizer (i.e., the hydrophilic first block) is anchored to the particle and cannot be redistributed between the particles. In our group, PISA has notably been used to form small particles of poly(methacrylic acid)-*b*-polystyrene (PMAA-*b*-PSty) (< 60 nm) by RAFT-mediated emulsion PISA.<sup>16, 17</sup> In the present work, crosslinked particles will be investigated, using either PMAA or poly(sodium 4-styrenesulfonate) (PSSNa) as macromolecular RAFT agent (macroRAFT).

## **2. Experimental section**

### **2.1. Materials**

Methyl methacrylate (MMA, Aldrich, 99%), styrene (Sty, Acros, 99%), methacrylic acid (MAA, Acros, 99.5%), ethylene glycol dimethacrylate (EGDMA, Aldrich, 98%), divinylbenzene (DVB,

Sigma Aldrich, 80%), sodium 4-styrenesulfonate (SSNa, Sigma Aldrich, > 90%), anionic surfactant (TA) (Disponil FES 32: ethoxylated fatty acid with a sulphate group) and non-ionic surfactant (TN) (Disponil A3065: ethoxylated fatty acid with a alcohol group), sodium dodecyl sulfate (SDS, Acros, 99%), ammonium persulfate (APS, Aldrich, 98%), sodium persulfate (NaPS, Sigma Aldrich, 99%), 4,4-azobis(4-cyanopentanoic acid) (ACPA, Aldrich, 98%), 1,3,5-trioxane (Sigma-Aldrich, 99.5%), and sodium hydrogen carbonate ( $\text{NaHCO}_3$ , Acros, 99%) were all used as received. 4-Cyano-thiothiopropylsulfanyl pentanoic acid (CTPPA) was synthesized following the protocol reported in the literature.<sup>17</sup> Water was deionized before use (Purelab Classic UV, Elga LabWater).

## 2.2. Methods

### 2.2.1. Synthesis of large size particles

*Step 1: Seed synthesis by batch emulsion polymerization.* In this step the seeds of larger particle population were prepared by batch polymerization (Table S1 of the Supporting information Material). In a jacketed glass reactor of 1 L to a heated mixture of 650 g of water, 0.1 g of Disponil FES 32 and 2 g of Disponil A3065 were added 85 g of MMA and 77 g of Sty. After the homogenization and deoxygenation by nitrogen bubbling for 30 min, 1.6 g of APS was added to initiate the polymerization reaction. The reaction system was kept at 80 °C under continuous agitation for 150 min. The regular withdrawal of samples allowed us to evaluate the conversion and particle size as a function of time.

*Step 2: Seeded semi-batch emulsion polymerization.* In semi-batch polymerization the latex was concentrated. In a 1 L glass reactor was added the latex obtained in the batch step, which was used as the initial charge in the reactor. With two syringe pumps were added to the reactor an initiator solution ( $150 \text{ g L}^{-1}$ ) and a pre-emulsion containing the mixture of water, Disponil FES 32, Disponil A3065, MMA and Sty. Table S2 in the Supporting information presents the formulation of the pre-emulsion. The regular withdrawal of samples allowed us to follow the monomer conversion as a function of time.

### 2.2.2. Synthesis of small size particles

PMAA-*b*-P(Sty-co-EGDMA) particles by PISA

*Step 1: PMAA MacroRAFT synthesis in water.* The synthesis of poly(methacrylic acid) (PMAA) macroRAFT agents was done following a procedure similar to the one described by Chaduc et al.<sup>17</sup>. 254 mg of CTPPA ( $2.5 \times 10^{-2}$  mol L<sup>-1</sup>), 25 mg of ACPA ( $2.5 \times 10^{-3}$  mol L<sup>-1</sup>), 3.13 g of MAA (0.99 mol L<sup>-1</sup>, *i.e.*, a targeted degree of polymerization of 40), 36.8 mL of deionized water and 546 mg of 1,3,5-trioxane ( $1.65 \times 10^{-1}$  mol L<sup>-1</sup>, used as an internal reference for NMR analysis) were placed in a three-neck round-bottom flask equipped with a condenser. After deoxygenation by freeze-pump-thaw method, the resulting mixture was immersed in an oil bath at 80 °C. This immersion in the oil bath corresponds to time zero of the polymerization. The polymerization was stopped at 270 min. The regular withdrawal of samples allowed us to follow the monomer conversion as a function of time and the evolution of molar masses and molar mass distributions as a function of monomer conversion. Table S3 gathers the features of the different batches of PMAA macroRAFT synthesized for this study.

*Step 2: Emulsion polymerization of styrene.* PISA was performed using a procedure similar to the one described by Chaduc et al.<sup>16</sup> 30 g of Sty, 33 g of the solution of the previously synthesized macroRAFT agent, 90.5 g of deionized water and 1.5 g of the EGDMA crosslinker were placed in a two-neck round-bottom flask equipped with a condenser. The mixture was deoxygenated by nitrogen bubbling for 30 min and was subsequently immersed in an oil bath at 80 °C. Then, 12 g of an aqueous solution of ACPA ( $2.54 \times 10^{-2}$  mol L<sup>-1</sup> neutralized by 3.5 mol equiv. of NaHCO<sub>3</sub>) were added to the reaction mixture, which corresponded to time zero of the polymerization. The regular withdrawal of samples allowed us to follow the monomer conversion as a function of time. The experimental conditions and main results of the PMAA macroRAFT mediated emulsion polymerizations are displayed in Table S4.

#### *PSSNa-b-P(Sty-co-DVB) particles particles by PISA*

*Step 1: PSSNa macroRAFT synthesis in water.* The synthesis PSSNa macroRAFT agent was based on the procedure described by Velasquez et al.<sup>18</sup> and is similar to one described above for PMAA synthesis. In a typical experiment, 250 mg of CTPPA ( $3.51 \times 10^{-2}$  mol L<sup>-1</sup>), 25 mg of ACPA ( $3.9 \times 10^{-3}$  mol L<sup>-1</sup>), 3.71 g of SSNa (0.7 mol L<sup>-1</sup>, *i.e.*, a targeted degree of polymerization of 20), 25.7 mL of deionized water and 550 mg of 1,3,5-trioxane (0.24 mol L<sup>-1</sup>) were added in the three-neck round-bottom flask. After deoxygenation by nitrogen bubbling, the polymerization was started by immersing the flask in an oil bath at 80 °C. The polymerization was stopped at 270 min. Again,

samples were withdrawn to monitor the evolution of monomer conversion as a function of time, and of molar masses and molar mass distributions as a function of monomer conversion. Table S5 gathers the features of the different batches of PSSNa macroRAFT synthesized for this study.

*Step 2: Emulsion polymerization of styrene.* 10 g of Sty, 11 g of PSSNa macroRAFT, 30.1 g of deionized water and 0.3 g of DVB were added in a two-neck round-bottom flask equipped with a condenser. The mixture was deoxygenated by nitrogen bubbling for 30 min and the flask was then immersed in an oil bath thermostated to 80 °C. Then, 4 g of an aqueous solution of ACPA ( $2.54 \times 10^{-2} \text{ mol L}^{-1}$  neutralized by 3.5 mol equivalent of  $\text{NaHCO}_3$ ) were added to the reaction mixture. The immersion in the oil bath corresponds to time zero of the polymerization. The regular withdrawal of samples allowed to follow monomer conversion as a function of time. The experimental conditions and main results of the PSSNa macroRAFT mediated emulsion polymerizations are displayed in Table S6.

#### *SDS-stabilized Poly(styrene-co-divinylbenzene) particles*

The synthesis of crosslinked small size particles was carried out by microemulsion polymerization, following the procedure reported by Moraes et al.<sup>19</sup> 152 g of styrene, 13 g of DVB (5 mol.% with respect to styrene), 30 g of SDS and 715 g of deionized water were placed in a jacketed glass reactor of 1 L equipped with reflux condenser and axial flow impeller forming a homogeneous initial mixture, cosurfactant was not used in the recipe. The dissolved oxygen was removed from the initial charge by bubbling nitrogen for 30 minutes. To start the polymerization reaction 0.75 g of NaPS was added. The reaction system was kept at 80 °C under continuous agitation for 150 min. The regular withdrawal of samples allowed to evaluate the conversion and particle size as a function of time.

#### ***2.2.3. Synthesis of bimodal high solids content latices***

For the synthesis of latices with a bimodal particle size distribution in semi-batch mode, a 500 mL jacketed glass reactor was used, where the seed latex, concentrated to a solid content between 55 and 57 wt.%, was added. A solution of APS and a pre-emulsion formed by the monomer mixture (MMA and Sty), TA, TN and the small particle latex were added to the reactor with two syringe pumps. Throughout the reaction aliquots were taken to evaluate the conversion evolution, solids



content, viscosity and particle size as a function of time. Tables S8, S9 and S10, in the Supporting Information, present the formulation of the pre-emulsion.

### 3. Characterization techniques

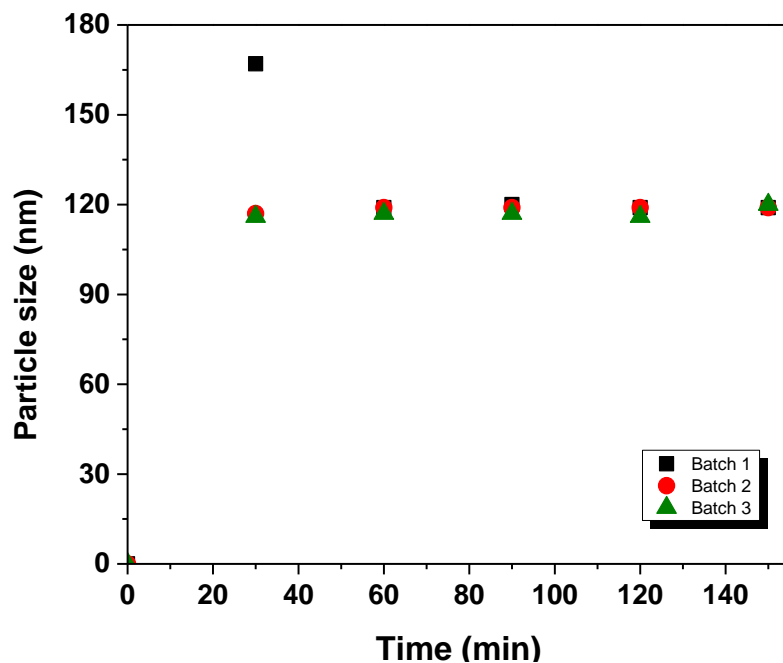
The conversion of MAA and SSNa was determined by  $^1\text{H}$  NMR spectroscopy in  $\text{D}_2\text{O}$  at room temperature (Bruker DRX 300) by the relative integration of the protons of the internal reference (1,3,5-trioxane) at 5.1 ppm and the vinylic protons of MAA (at 5.6 and 6.0 ppm) or SSNa (at 5.4 and 5.9 ppm). Size exclusion chromatography (SEC) measurements were performed in THF at 40 °C, at a flow rate of 1 mL min $^{-1}$ . Before analysis, the polymers were modified by methylation of the carboxylic acid groups using trimethylsilyldiazomethane. They were analyzed at a concentration of 3 mg mL $^{-1}$  after filtration through a 0.45  $\mu\text{m}$  pore size membrane. The separation was carried out on three Polymer Laboratories columns [3  $\times$  PLgel 5  $\mu\text{m}$  Mixed C (300  $\times$  7.5 mm) and a guard column (PL gel 5  $\mu\text{m}$ )]. The setup (Viscotek TDA 305) was equipped with a refractive index (RI) detector ( $\lambda = 930$  nm). The average molar masses (number-average molar mass ( $M_n$ ) and mass-average molar mass ( $M_w$ )) and the molar-mass dispersity value ( $D = M_w/M_n$ ) were derived from the RI signal by a calibration curve based on poly(methyl methacrylate) standards with  $D$  close to 1.0. The emulsion polymerization conversion was determined by gravimetry. Transmission electron microscopy (TEM) images were obtained from a Philips CM120 electron microscope device operating at a voltage of 100 kV. The samples were prepared by drying a drop of diluted sample on a carbon/Formvar coated copper grid (Ted Pella, Inc.). The intensity-weighted mean diameter (or Z-average diameter),  $Z_{\text{ave}}$ , of the latex particles was measure by dynamic light scattering (DLS) technique on a Malvern Nano Zetasizer instrument. The samples were diluted in deionized water and analyzed in triplicate. The viscosity of the latex was determined on a rheometer Thermo Scientific HAAKE MARS at a shear rate of 20 s $^{-1}$ .

## 4. Results and discussion

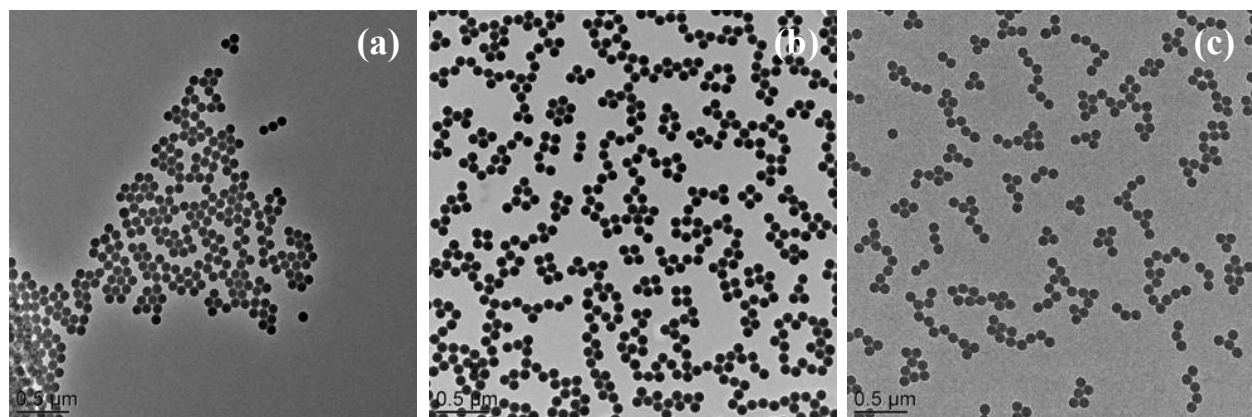
### 4.1. Synthesis of large size particles

The seed latex with a 20 wt.% solids content was obtained through batch emulsion polymerization, followed by a semi-batch starved feed process. The initial batch mixture contained monomer, anionic (TA) and nonionic (TN) surfactants. DLS measurements showed that the average seed particle size was approximately 120 nm (Figure 1), which corresponds to a

$N_p = 1.8 \times 10^{17}$  particles per liter with  $Z_{ave}$  less than 0.1, indicates latices with narrow PSD, which is confirmed by the TEM images in Figure 2.



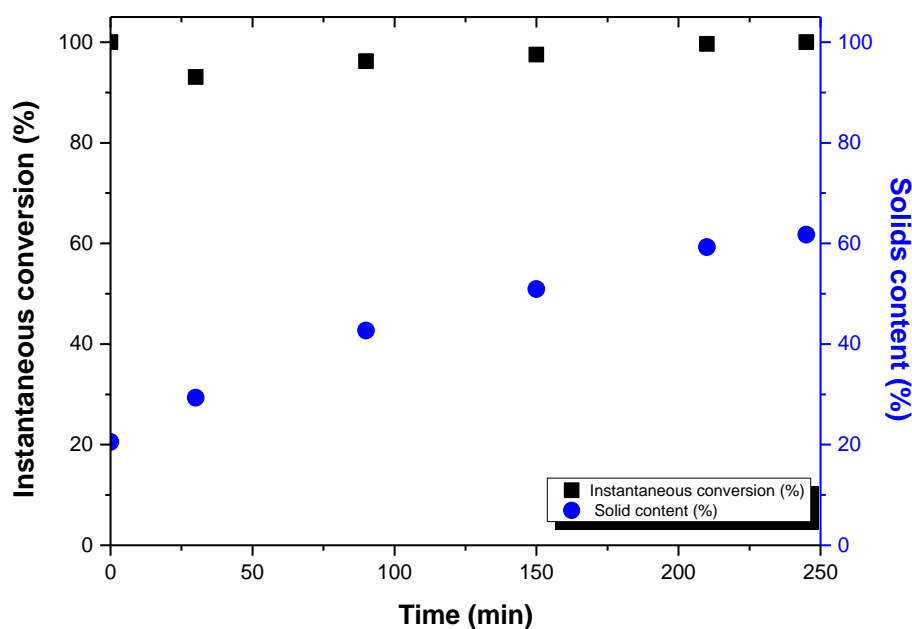
**Figure 1.** Evolution of particle diameter as a function of time. The experimental conditions for Batch 1 to Batch 3 are shown in Table S1.



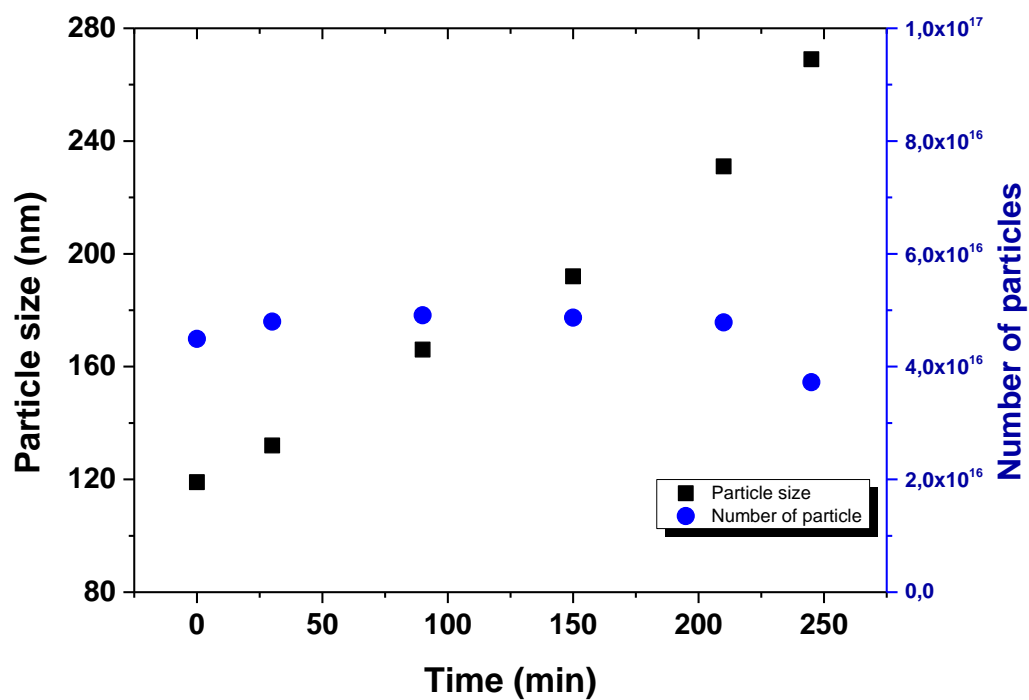
**Figure 2.** TEM images of the polymer particles from batch polymerization, (a) Batch 1, (b) Batch 2 and (c) Batch 3. The experimental conditions for Batch 1 to Batch 3 are shown in Table S1.

As the pre-emulsion is added to the medium, APS is also injected in order to ensure that the conversion is maximal throughout the entire polymerization reaction. As can be seen in Figure 3, the addition of pre-emulsion and APS solution were adequate to ensure that the instantaneous conversion remained close to 100% throughout the reaction, ensuring starved monomer conditions.

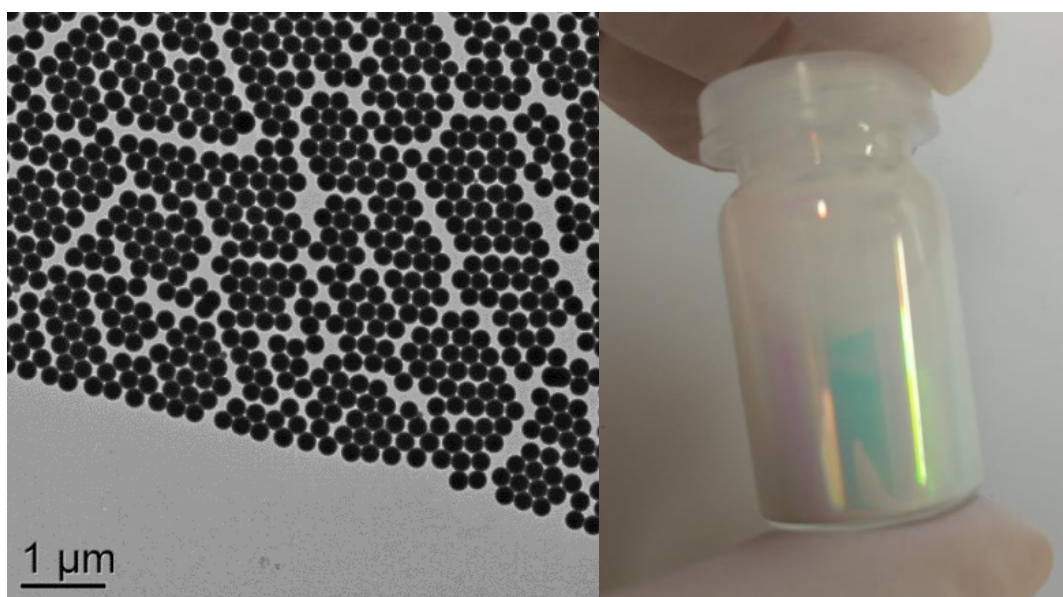
In this manner we were able to reach solid contents of approximately 60 wt.%, with a particle diameter on the order of 270 nm (LP1) (Figure 4). The number of particles remains practically constant throughout the reaction, which suggests that the medium is stable without the formation of coagulum. There is a small decrease in the number of particles and a corresponding increase in the average diameter after 200 minutes, indicating that there is a controlled coagulation of the particles. The TEM image in Figure 5a shows that the particles are spherical and very regular in size, and this is confirmed by the iridescence seen in Figure 5b.



**Figure 3.** Evolution of instantaneous conversion and solids content with the reaction time for latex LP1 (Table S2).

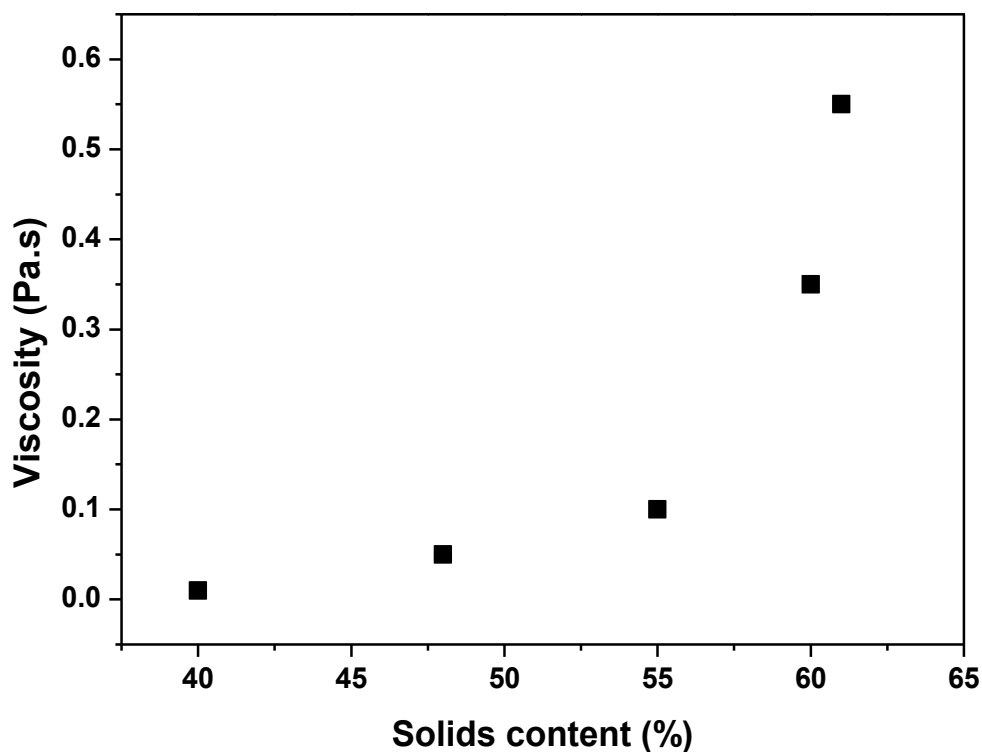


**Figure 4.** Evolution of number of particles and particles diameter with the reaction time for LP1 (Table S2).



**Figure 5.** TEM image of latex particles of LP1 (Table S2) and the iridescent effect.

Figure 6 shows the evolution of the viscosity of the latex with increasing solids content. Very low viscosity values are observed till solids content around 50 wt.%. As expected, a significant increase in latex viscosity is observed between 55 wt.% and 60 wt.%. Nevertheless the viscosity of the latex was about 0.6 Pa.s at a shear rate of  $20\text{ s}^{-1}$ .



**Figure 6.** Evolution of the latex viscosity of LP1 (Table S2) as a function of the solids content at a shear rate of  $20\text{ s}^{-1}$ .

#### 4.2. Synthesis of small particles

Two different approaches were adopted for the synthesis of the small size crosslinked particles: either the PISA strategy or the process developed by Moares.<sup>19</sup>

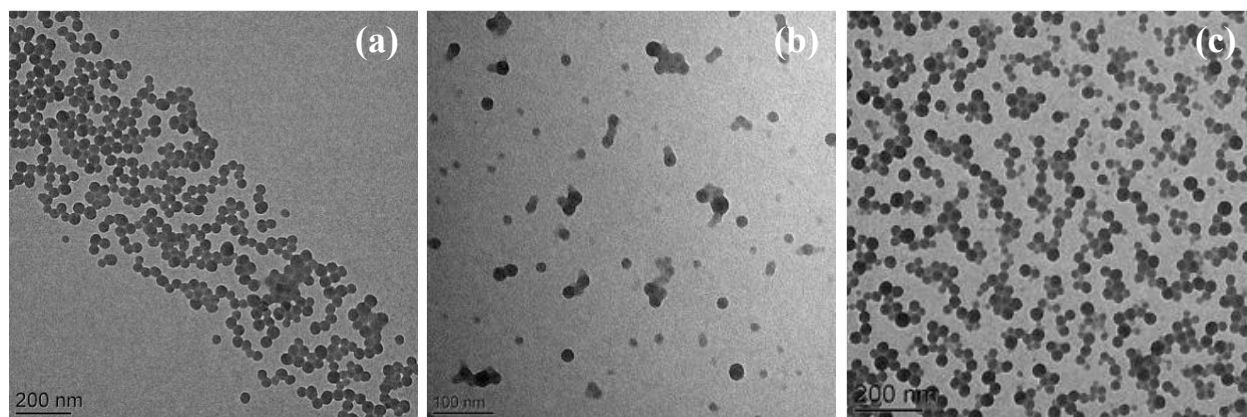
In this step, it is necessary to have small crosslinked particles because crosslinking reduces significantly the swelling capacity of the polymer particles, preventing their growth in the synthesis step of high-solids bimodal latices.<sup>11,20</sup>

#### *4.2.1 PMAA- and PSSNa stabilized crosslinked particles by the PISA strategy*

The synthesis of PMAA and PSSNa macroRAFT were performed in water at 80 °C using CTPPA as RAFT agent and ACPA as initiator.<sup>17, 18</sup> For both types of macroRAFT, the targeted molar mass was around 4000 g.mol<sup>-1</sup>. All the experimental conditions and features of the different batches of macroRAFTs synthesized for this study are gathered in the Supporting information (Tables S3 and S5 and Figures S1, S2 and S4). The three MAA polymerizations are reproducible and present all the features expected from a controlled process with a linear increase of molar masses with conversion (Figure S2) leading to polymer chains with well-defined molar mass and low dispersity (below 1.20) (Table S3). For the three PSSNa macroRAFTs syntheses too, the conversion versus time profiles also showed a very good reproducibility of the process (Figure S4). The determination of the experimental molar mass of the PSSNa macroRAFT requires analyses by aqueous size exclusion chromatography or by MALDI-TOF spectrometry. Such characterization could not be undertaken in the present work, but relying on our previous studies<sup>14–20</sup> we can expect good control of the polymerization, leading to the well-defined PSSNa macroRAFT. Using final conversion, theoretical molar masses were thus estimated (Table S5).

Synthesis of the crosslinked PS particles via PISA was first conducted with the PMAA macroRAFT. The latter was mixed with styrene, EGDMA (2.0 mol.% with respect to styrene) as crosslinking agent and ACPA as initiator (see Tables S4 and S6 for the experimental conditions of these emulsion copolymerizations). Full conversion was reached in about 90 min, after an induction period of 30 min. The induction period corresponds to the time required for the poly(styrene-*co*-EGDMA) block to reach a critical chain size which leads to self-assembly of the chains forming the particles. After nucleation, the particles are swollen with the residual monomers and the polymerization takes place inside these particles, which results in a sudden increase in the reaction rate. It is worth noting that the addition of EGDMA did not prevent the self-assembly, as already observed in a similar system,<sup>21</sup> which can likely be attributed to the different reactivity of the two double bonds of the crosslinker allowing assembly before significant crosslinking of the chains.<sup>21</sup> In addition, the self-assembly of the chains before significant crosslinking can also be attributed to delayed gelation of controlled radical polymerizations systems compared to conventional system, as reported by Hamzehlou et al.<sup>22</sup> . Indeed, small size particles (around 30 nm by DLS, Table S4), consistent with a PISA process, were obtained.

Emulsion copolymerization of styrene and DVB (2 mol.% with respect to styrene) was then performed in the presence of PSSNa macroRAFT (Table S6). A longer induction period of about 60 min was observed (Figure S5). Again, the self-assembly is not prevented by the presence of DVB. Indeed, taking into account the high reactivity of the first double bond of DVB<sup>23</sup> and considering that the second double bond should have approximately the same reactivity as styrene,<sup>24, 25</sup> the hydrophobic block is able to reach the critical molar mass leading to self-assembly without significant crosslinking. After nucleation, the polymerization is slower than in the PMAA/Sty/EGDMA system (Figure S5). The final particle sizes close to 35-40 nm by DLS are similar to the ones obtained with PMAA, and consistent with the PISA process. For both systems, TEM images confirm that small spherical particles are obtained. So, the PISA approach confirmed to be a valuable approach for the formation of the small and crosslinked PS particles sought for the formation of the high solids content bimodal latices.



**Figure 7.** TEM images of (a) PMAA-*b*-P(Sty-*co*-EGDMA) particles (PISA 1), (b) PSSNa-*b*-P(Sty-*co*-DVB) particles (PISA-SSNa 1) and SDS-stabilized P(Sty-*co*-DVB) particles (PC1). The experimental conditions for these experiments are shown in Tables S4, S6 and S7 of Supplementary Material.

#### 4.2.2. SDS-stabilized P(Sty-*co*-DVB) particles by microemulsion polymerization

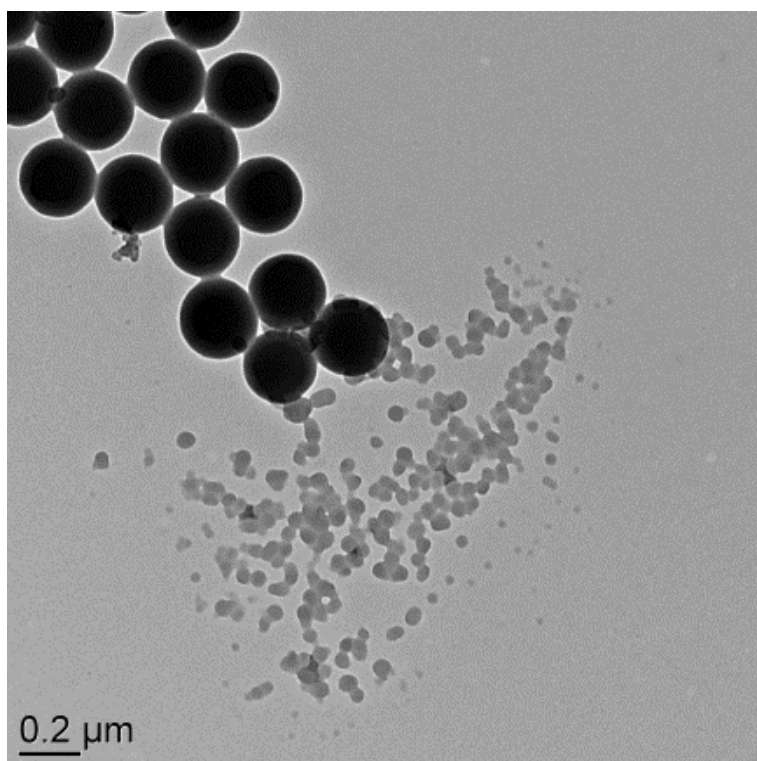
The synthesis of P(Sty-*co*-DVB) particles was performed in water at 80 °C by emulsion polymerization using sodium dodecyl sulfate as surfactant and sodium persulfate as initiator. The polymerization reached 100% of conversion very quickly (around 60 min, Figure S6), as could be

expected from a previous study.<sup>9</sup> The obtained latex was fluid, with a particle diameter of 35 nm, and morphology that is quite similar to the PISA particles presented before.

#### 4.3. Synthesis of bimodal high solids content latices

For the synthesis of bimodal latices, large particle latex with high solids content was used as the initial charge in the reactor and different amounts of pre-emulsion containing the small particles were added in semi-batch mode. As was observed earlier, the latex viscosity increases significantly up to 60 wt.%, so in this step, the solids content of large particle latices were adjusted between 55 and 59 wt.%.

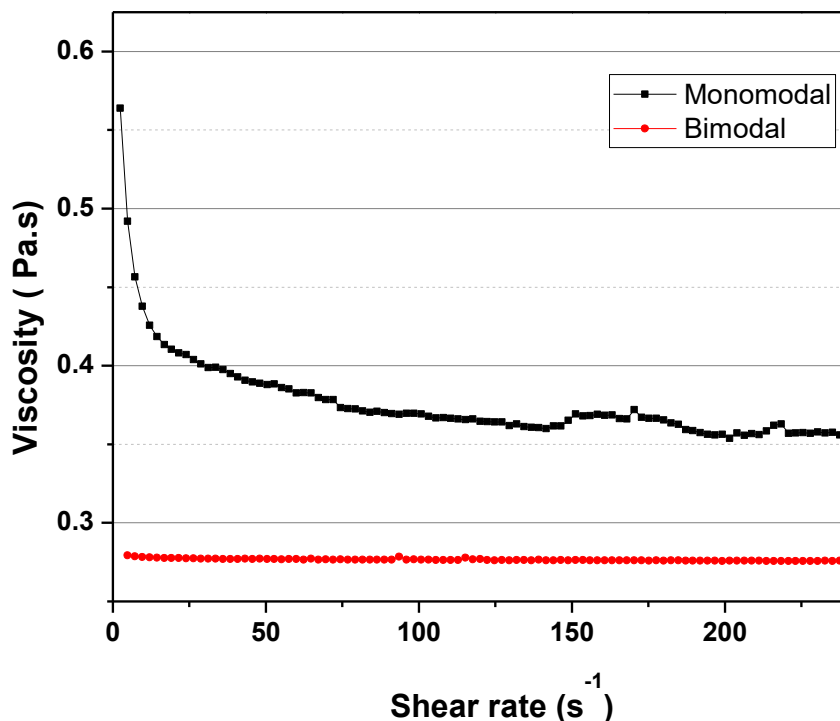
Initially, the reactor was fed with a latex consisting of monodisperse particles, with an average diameter of 242 nm and a solid content of 57 wt.% (LP2). Then, by semi-batch method, the reactor was fed with a pre-emulsion containing the PMAA-*b*-P(Sty-co-EGDMA) small particles, to obtain a bimodal latex (BL1). In the TEM image showed in Figure 8 can be observed the two particle populations.



**Figure 8.** TEM image of bimodal latex BL1 (Table S8 of the Supplementary Material) with 60 wt.% SC from PMAA-*b*-P(S-co-EGDMA) small particles.



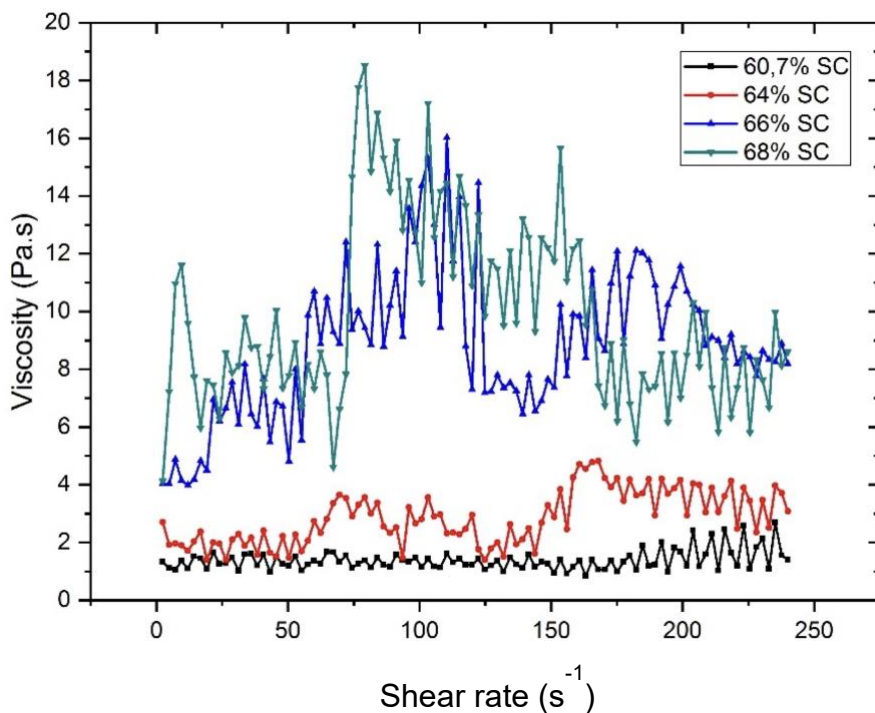
The viscosity comparison between bimodal and monomodal latices with the same solid content (Figure 9), highlights the influence of the small particle presence in latices viscosity. The addition of a second particle population leads to a decrease in the viscosity, as well as in the shear-sensitivity of the viscosity.



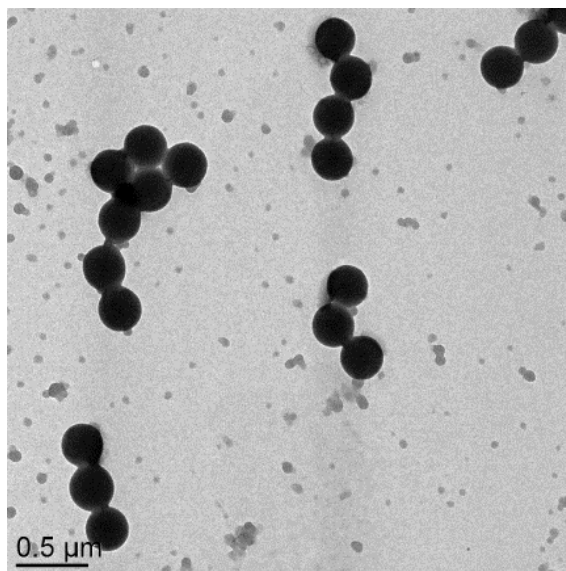
**Figure 9.** Viscosity of the latex BL1 (Table S8 of the Supplementary Material) with 60 wt. % of solids content.

Unfortunately, it was not possible to obtain latex with solid content above 60 wt.% as the system rapidly became destabilized. This might be due to a stability problem concerning the PMAA-*b*-P(S-*co*-EGDMA) small particles. It is known from literature that there is a sharp change in PMAA chain conformation from hypercoil to rod-like conformation around pH 5.<sup>17</sup> So, in order to get around this situation, the pH of the reactor initial charge was adjusted from 2 to 9 with NaOH solution 1N, and the pre-emulsion was adjusted to 7.7. The adopted pH-adjustment strategy contributed to latex stabilization and resulted into a 68 wt.% solids content product (experiment

BL2 in Table S8 of the Supplementary Material). However, the main limitation was the high viscosity values - approximately 6 Pa.s. So, to go further on, it was decided to stop the reaction around 65 wt.% solids content. According to the viscosity profile shown in Figure 10, viscosity values at 65 wt.% are still around 2.0 Pa.s.



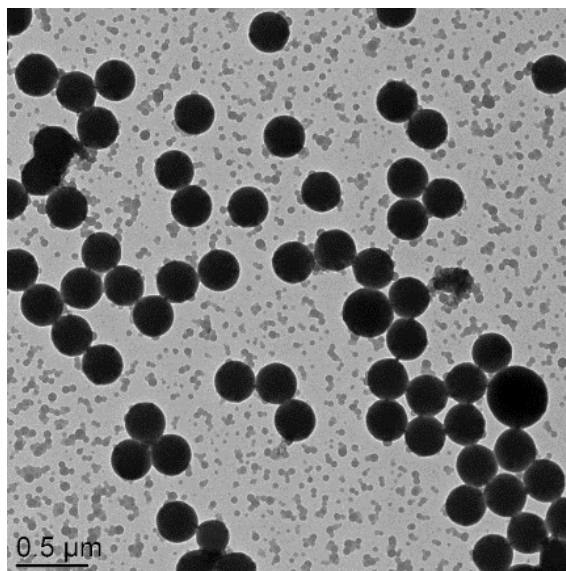
**Figure 10.** Latex viscosity variation throughout the polymerization reaction due to the increase in the solids content for experiment BL2 (Table S8 of the Supplementary Material).



**Figure 11.** TEM image of bimodal latex with 65 wt.% SC from PMAA-*b*-P(S-*co*-EGDMA) small particles after the pH increase for experiment BL3 (Table S8 of the Supplementary Material).

For comparative purposes, a bimodal latex with 65 wt.% SC was obtained using regular large size particles and crosslinked SDS-stabilized P(Sty-*co*-DVB) small particles (Figure 12). Those crosslinked particles have already been reported in the literature by Moraes et al.<sup>9</sup>. Viscosity test suggests that, for a 65 wt.% solids content product, experiment BL5 (Table S9 of the Supplementary Material) exhibits lower viscosity values (around 1.4 Pa.s) than lattices BL4 (Table S8 of the Supplementary Material), previously obtained with PMAA-*b*-P(Sty-*co*-EGDMA) small particles (around 2 Pa.s) (Figure S5 of the Supplementary Material).

The difference between the viscosity results revealed by the compared reactions may be due to the PMAA conformation, as discussed above. PMAA chain structures shows a rod conformation when the pH of the medium is up to 5 ( $\sim pK_a = 4.65$ ). Thus, it is possible that this conformational change affects the small particles size – or even its effective hydrodynamic volume, which increases the interaction between particles and may be responsible for a higher viscosity profile.



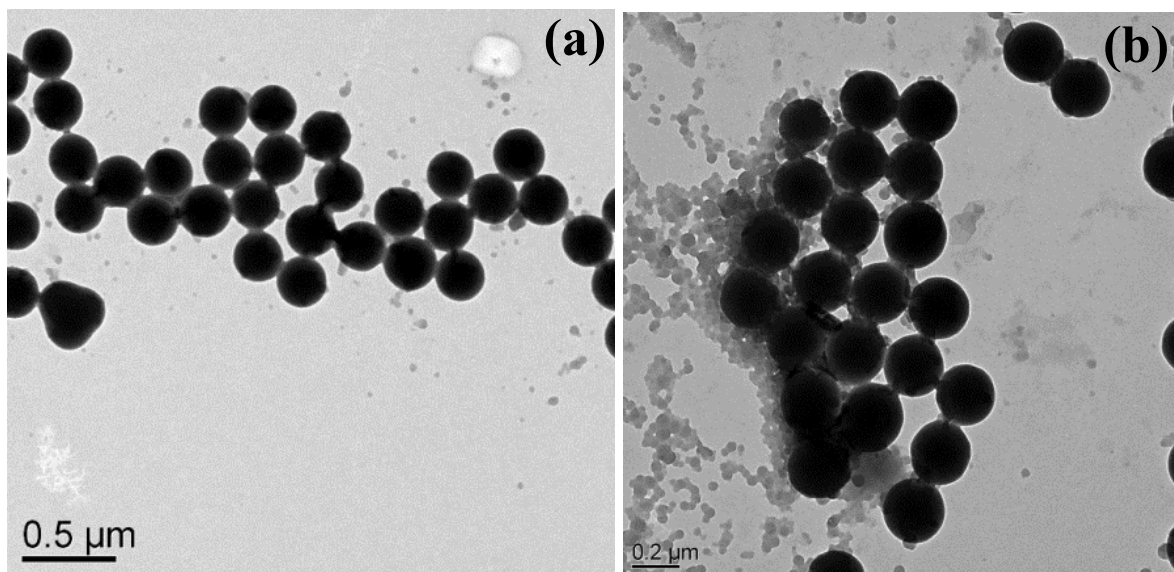
**Figure 12.** TEM image of bimodal latex with 65 wt.% SC from SDS- stabilized P(Sty-*co*-DVB) small particles for experiment BL5 (Table S9 of the Supplementary Material).

Even though the bimodal latex composed by crosslinked small particles tends to exhibit lower viscosity values (which is desirable for the purposes of the latices presented in this paper), it is necessary to take into account how advantageous is to make particles without surfactant into a process, regarding not only environmental but also in terms of product quality. For example, if the latex is used to form waterborne coatings, the mobility of the low molar mass surfactant in the film, during the drying process and later on, can lead to clumps of surfactant at the film-air interface and also within the film, creating hydrophilic channels that can carry water through the polymeric film, thus affecting its barrier properties.<sup>26</sup>

Given the size differential the small particles present a very large surface area, meaning that if made by conventional emulsion polymerisation a certain amount of surfactant is required to ensure their creation and stabilisation. Thus, the ability to develop a population of small particles with a predetermined size without surfactant allows us to significantly reduce the amount of the latter in the final product.

Two experiments were prepared using the same formulation, but adjusting different pHs at the reaction medium, to evaluate how the pH could affect the results. For experiment BL6, the pH of the reactor initial charge (LP8) was adjusted from 2 to 9 with NaOH solution 1N, and the pre-

emulsion was adjusted to 7.7. On the other hand, BL7 was performed without any NaOH addition. The TEM images of the two final latices are shown in Figure 13.



**Figure 13.** TEM image of bimodal latex (a) For BL6 with pH 9 and (b) BL7 with pH 2. The experimental conditions for BL6 and BL7 are presented in Table S10 of Supplementary Material.

There was no significant difference between the two experiments in terms of average particle size calculated with TEM and solids content, which suggests that the pH adjustment is not necessary or will not exert huge influence as a synthesis parameter. In fact, both experiments were designed to achieve 65 wt.% SC after 6 hours of reaction. However, after 3 hours of reaction, both systems started to lose their stability and the formation coagulum was observed. Thus, the obtained results correspond to the withdrawn samples at 180 minutes of reaction. Both materials presented viscosity values around 2.0 Pa.s at solid contents of 63 wt. %.

## Conclusion

Latices with two particle populations were synthesized via emulsion polymerization in a semi-batch process, where the reactor containing the large particle latex was fed with a pre-emulsion containing small particles obtained via RAFT-mediated PISA. For the same solid content, the viscosity of monomodal latex is higher than that of bimodal latices, thus, the particle size distribution influences the viscosity of the latex. The ionic strength of the reaction medium influences the stability of the latex and can induce coagulation of the particles, especially if the

latex is obtained without the addition of surfactants. The stability of the latex obtained from PMMA-stabilized small particles depends on the pH of the medium and is favored by the increase in pH.

“The comparison of viscosity between the 65 wt.% SC latex containing crosslinked SDS-stabilized P(Sty-co-DVB) as small particles and the 65 wt.% SC latex containing PMAA-b-P(Sty-co-EGDMA) small particles shows that the use of a surfactant improves latex stability and decreases viscosity.

Comparison of the two strategies followed to obtain latices with high solids content using small surfactant-free particles clearly shows that the hydrophilic block influences the stability of the latex. The route that uses PMAA-b-P(Sty-co-EGDMA) as small particles allowed us to achieve solid contents of 68 wt.%, but the final latices had viscosities greater than the limit of 2 Pa.s. Nevertheless, comparing samples of the two routes that present viscosity values of 2 Pa.s shows that the route using the PMAA-stabilized small particles prepared by PISA presented higher solids content values (65wt.% vs. 63 wt.% solids content for PSSNa-stabilized small particles) and better long term stability than lattices with PSSNa-stabilized small particles.

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