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# Effect of in-Situ-Produced Block Copolymer on Latex Particle Morphology

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ABSTRACT: A strategy to modify the latex particle morphology by means of block copolymers produced in-situ by controlled radical polymerization (CRP) is presented. The strategy consisted in adding during the formation of the seed a small amount of a CRP agent, so that at the end of the seed formation some of the polymer chains were capped with the CRP agent. Polymerization of the second stage monomer in the presence of additional initiator led to the formation of some block copolymer chains that help to compatibilize the two polymers. This strategy substantially affected particle morphology. The effect of the proposed strategy on particle morphology was analyzed in terms of the underlying thermodynamic and kinetic factors.

## Introduction

The production of composite latex particles with defined morphology is a problem of great technical interest as they have a broader spectrum of application properties than particles having uniform composition, and hence they play an important role in coatings, adhesives, impact modifiers, and many other materials.[1] Composite latex particles are commonly prepared by seeded semicontinuous emulsion polymerization. A preformed latex (polymer 1) is swollen with a certain amount of monomer 2, and polymerization is started by adding initiator. Polymerization leads to the formation of chains of polymer 2 in a matrix of polymer 1 swollen with monomer 2. Because of the incompatibility between the two polymers, phase separation occurs and clusters of polymer 2 are formed within the matrix of polymer 1. Polymerization continues in both clusters and matrix, and hence the clusters grow in size and new clusters are formed. In addition, van der Waals forces cause cluster migration toward the equilibrium morphology.[2−4] Depending on the polymerization conditions, a wide variety of particle morphologies can be produced: core−shell,[5] "inverted" core−shell,[6] hemispheres,[7] "raspberry-like,[8] and void particles.[9]

Particle morphology depends on the interplay between thermodynamics and kinetics.[1−4,10,11] Thermodynamics determines the particle morphology at equilibrium according to the minimum surface free energy. Kinetic factors control whether the particle reaches the equilibrium morphology or remains at a metastable (kinetically stable) morphology.

The polymer−polymer and polymer−aqueous phase interfacial tensions play a key role in the development of the particle morphology as they determine the surface free energy (Figure 1). In addition, they strongly affect the kinetics. The driving forces for cluster migration toward the equilibrium morphology are the van der Waals forces among clusters and between clusters and aqueous phase. These forces are related to the interfacial tensions.[12] The lower the interfacial tensions, the lower the van der Waals forces and hence the slower the evolution of the morphology toward equilibrium.

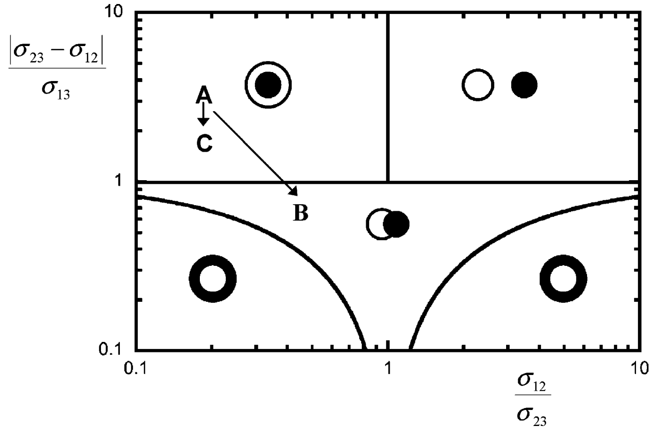

**Figure 1.** Equilibrium morphologies: ○, polymer 1 (seed); ●, polymer 2 (produced by polymerization of the second stage monomer) (adapted from ref 2).

Polymer−aqueous phase interfacial tensions are affected by the hydrophilicity of the polymers,[13] the initiator end groups,[14] the type and amount of surfactant,[15] and the presence of functional monomers.[13] The polymer−polymer interfacial tension is more difficult to modify. Rajatapiti et al.[16] used graft copolymers to lower this interfacial tension. The process that they used was as follows. First, a minimemulsion of butyl acrylate containing a methyl methacrylate macromonomer was formed. Polymerization of this miniemulsion led to the formation of the poly(butyl acrylate) seed with poly(butyl acrylate)-*graft*-polymethacrylate copolymers. Polymerization of methyl methacrylate on this seed led to composite PBA/PMMA particles. The authors showed that morphology was severely affected by the presence of the graft copolymer. This approach requires that an adequate macromonomer is available. In addition, the incorporation of the macromonomer into the seed would be difficult for processes other than miniemulsion polymerization.[17−19]

The objective of this article is to explore the possibility of modifying the latex particle morphology by means of block

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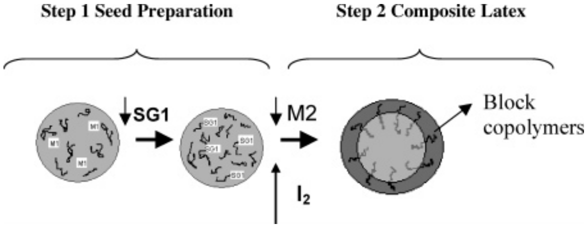
**Scheme 1. Polymerization Steps To Control the Particle Morphology by Nitroxide-Mediated Polymerization**



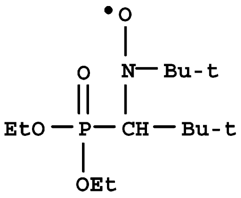
copolymers produced in-situ by controlled radical polymerization (CRP). These block copolymers can reduce the polymer–polymer interfacial tensions affecting both the equilibrium morphology and the kinetics of phase migration.

## Polymerization Strategy

The polymerization strategy is summarized in Scheme 1. It includes the following steps:

1. Polymerization of monomer 1 in an aqueous dispersed medium. This polymerization may be conventional emulsion polymerization or miniemulsion polymerization (method used in this work). At a moment during polymerization, a modest amount of CRP agent is added. In principle, there are no limitations with respect of the type of CRP agent. In this work, *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, Scheme 2) kindly supplied by Arkema was used. In principle, only a small fraction of block copolymers is required, and hence the amount of SG1 is significantly lower than the quantity employed in formulations where the polymerization is fully controlled.[20] Ideally, most of the polymer chains should be formed as if SG1 were not present. Therefore, a relatively high initiator/SG1 ratio is used. The nitroxide could be added at any moment during polymerization of monomer 1. At the

**Scheme 2. *N*-*tert*-Butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) Nitroxide, SG1**[a]



[a] The nitroxide agent used in the in-situ production of block copolymers.

**Table 1. Composite PMMA/PS Latexes Synthesized**

| | step 1 | | step 2 | | (co)polymer | rel interfacial tensions[a] | mol wt |
|---|---|---|---|---|---|---|---|
| latex1 | batch miniemulsion polymerization of MMA in the presence of SG1 (Table 2); $X_{MMA} = 0.79$ | | swelling the MMA latex (130 g) with styrene (7 g), overnight at room temperature | heat to 90 °C; AIBN (0.18 g) dissolved in styrene (7 g) added; polymerization in batch | S-rich poly(S-*co*-MMA) random copolymer + poly (MMA-*block*-S-*co*-MMA) | $\sigma_{12}$: lowest;<br>$\sigma_{13}$: medium (KPS);<br>$\sigma_{23}$: higher (AIBN) | lowest |
| latex 2 | batch miniemulsion polymerization of MMA (Table 2); $X_{MMA} = 0.89$ | | swelling the MMA latex (130 g) with styrene (7 g), overnight at room temperature | heat to 90 °C; AIBN (0.18 g) dissolved in styrene (7 g) added; polymerization in batch | S-rich poly(S-*co*-MMA) random copolymer | $\sigma_{12}$: low;<br>$\sigma_{13}$: medium (KPS);<br>$\sigma_{23}$: highest (AIBN) | high |
| latex 3 | batch miniemulsion polymerization of MMA in the presence of a CTA (Table 2), $X_{MMA} = 0.96$ | | swelling the MMA latex (130 g) with styrene (7 g), overnight at room temperature | heat to 90 °C; AIBN (0.18 g) dissolved in styrene (7 g) added; polymerization in batch | PS | $\sigma_{12}$: low;<br>$\sigma_{13}$: medium (KPS);<br>$\sigma_{23}$: highest (AIBN) | lowest |
| latex 4 | batch miniemulsion polymerization of MMA (Table 3); when conversion was ca. 15%, SG1 was added; SG1/[initiator] = 0.3 (mol/mol); $X = 0.7$ | all MMA removed by devolatilization | swelling the MMA latex (130 g) with styrene (7.1 g), overnight at room temperature | heat to 90 °C and kept for 4 h; AIBN (0.22 g) dissolved in styrene (10.6 g) added; 15 min later another shot of styrene (10.5 g) | PS+poly(MMA-*block*-S) | $\sigma_{12}$: lowest;<br>$\sigma_{13}$: high(AIBN);<br>$\sigma_{23}$: highest (AIBN) | low |
| latex 5 | batch miniemulsion polymerization of MMA; $X_{MMA} = 1$ | no devolatilization needed as complete conversion was achieved | swelling the MMA latex with styrene, overnight, room temperature | heat to 90 °C and kept for 4 h; AIBN (0.22 g) dissolved in styrene (10.6 g) added; 15 min later another shot of styrene (10.5 g) | PS | $\sigma_{12}$: low;<br>$\sigma_{13}$: high (AIBN);<br>$\sigma_{23}$: highest (AIBN) | high |
| latex 6 | batch miniemulsion polymerization of MMA in the presence of CTA; $X_{MMA} = 0.97$ | | swelling the MMA latex with styrene, overnight, room temperature | heat to 90 °C and kept for 4 h; AIBN (0.22 g) dissolved in styrene (10.6 g) added; 15 min later another shot of styrene (10.5 g) | PS | $\sigma_{12}$: low;<br>$\sigma_{13}$: high (AIBN);<br>$\sigma_{23}$: highest (AIBN) | low |

[a] The values of interfacial tensions are all on a relative scale: lowest ($\sigma_{12}$ with block copolymers) → low → medium → high → highest ($\sigma_{23}$).

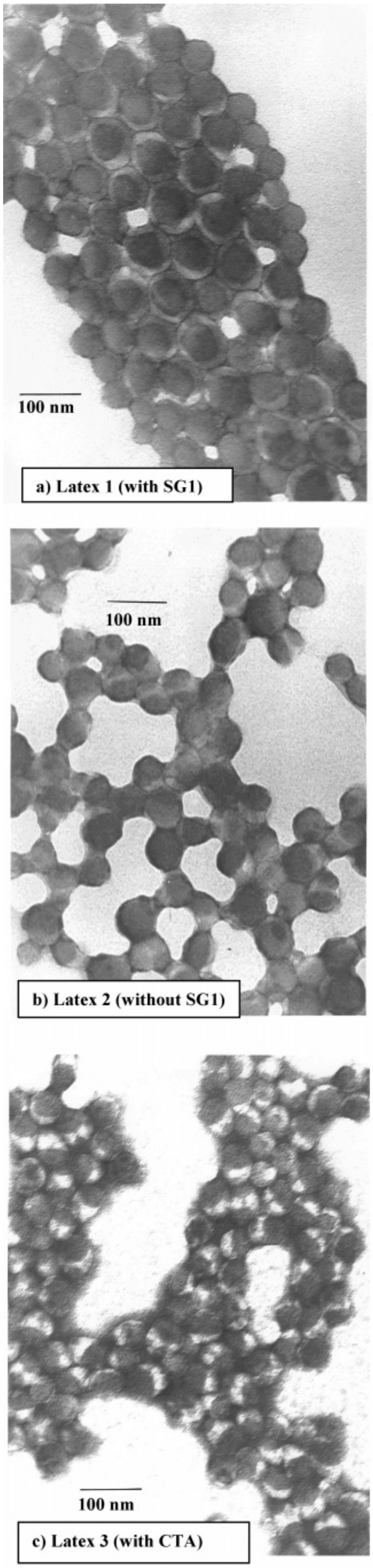


**Figure 2.** TEM micrographs of PS/PMMA composite particles stained with PTA and $RuO_4$.

**Table 2. Recipe Used To Prepare the PMMA Seed for Latexes 1−3 Using SG1 at 50 °C**

| ingredients | amount (g) |
|---|---|
| MMA | 21 |
| $K_2S_2O_8$ | 0.36 |
| $Na_2S_2O_5$ | 0.25 |
| hexadecane | 1.75 |
| SDS | 0.91 |
| $NaHCO_3$ | 0.39 |
| CTA (only in latex 3) | 0.06 |
| water | 181.8 |
| SG1/[initiator] = 0.1 (mol/mol) | |

**Table 3. Recipe Used To Prepare the PMMA Seed for Latexes 4−6 Using SG1 at 60 °C**

| ingredients | amount (g) |
|---|---|
| MMA | 225 |
| AIBN | 2.25 |
| hexadecane | 15.65 |
| SDS | 6.65 |
| $NaHCO_3$ | 2.30 |
| CTA (only in latex 6) | 0.60 |
| water | 525 |
| SG1/AIBN = 0.3 (mol/mol)[a] | |

[a] The SG1 was added as a shot at ca. 15% conversion.

end of step 1, dead chains of polymer 1 form the major part of the polymer particle. In addition, some chains of polymer 1 capped with SG1 ($Pol_1$-SG1) are present. Because of the large excess of initiator, the $Pol_1$-SG1 will have a broad molecular weight distribution with an average chain length close to the kinetic chain length.

2. Monomer 2 is added together with additional initiator (if needed). When the $Pol_1$-SG1 dormant chains dissociate into active polymer chains and nitroxide radicals, the polymer chain would react with monomer 2, yielding a block copolymer. Because of the high concentration of radicals, the nitroxide radicals likely react with polymer 2 radicals, resulting from decomposition of the initiator. It is expected that the polymer 2 block will have a broad MWD with an average chain length close to the kinetic chain length. Therefore, this method will lead to a block copolymer with a wide composition distribution as it results from a random combination of two polymers, each of them with a given MWD.

## Experimental Part

**Materials.** Styrene and methyl methacrylate monomers were washed with a 10% aqueous sodium hydroxide solution to remove the inhibitor before use. After that, calcium chloride anhydrous ($CaCl_2$) was added to remove all remaining water, and then, the monomers were stored in a refrigerator until use. The initiators, potassium persulfate ($K_2S_2O_8$, Aldrich), sodium metabisulfite ($Na_2S_2O_5$, Aldrich), azobis(isobutyronitrile) (AIBN, Aldrich); the polystyrene ($M_w = 280\,000$, Aldrich); the buffer, sodium hydrogen carbonate ($NaHCO_3$, Aldrich); the surfactant, sodium dodecyl sulfate (SDS, Aldrich); the chain transfer agent, *tert*-dodecylmercaptan (CTA, Fluka); and the costabilizer, hexadecane (Aldrich), were used as received. The CRP agent, *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), was kindly supplied by Arkema.

**Latex Preparation.** Table 1 summarizes the PMMA/PS latexes synthesized. The seed of latex 1 was prepared in the presence of SG1. A low SG1/initiator ratio (0.1 mol/mol) was used; therefore, the polymerization was not controlled. The aim was to have at the end of the polymerization a sufficient number of PMMA chains capped with SG1, which were extended in the subsequent polymerization of styrene. Because the conversion reached at the end of the seed preparation was not complete ($X_{MMA} = 0.79$), in addition to the block copolymers styrene-rich poly(styrene-*co*-methyl methacrylate) random copolymers were produced during stage 2. Latex 2 was a reference latex produced following the same procedure as

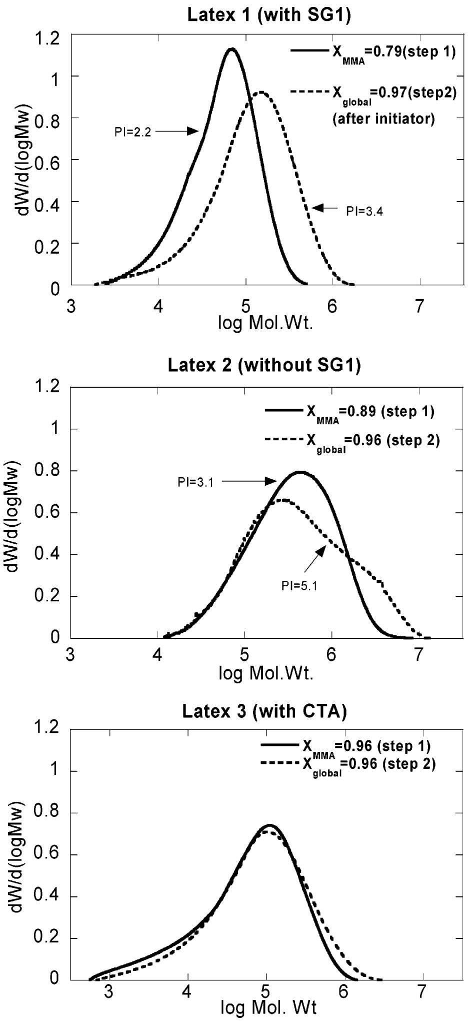


**Figure 3.** MWD of the seed and final polymer for latexes 1−3.

in latex 1 but without SG1. This latex had a molecular weight substantially higher than that of latex 1; latex 3 was produced using the same procedure as in latex 1, but using a CTA instead of SG1 in order to synthesize a latex with a molecular weight similar to latex 1. To influence less the molecular weight of the seed, in the preparation of latex 4, the addition of SG1 was delayed until the monomer conversion was 15% (see Table 3 for details). Total conversion was not achieved and MMA was removed by devolatilization. The amount of MMA removed was taken into account to add the adequate amount of styrene so that the final overall composition of the latex was 50/50. Latex 5 was a reference latex prepared as latex 4 but not using SG1. It presented a molecular weight higher than that of latex 4. Latex 6 was prepared as latex 4, but using a CTA instead of SG1 (Table 3).

**Latex Characterization.** Monomer conversion was determined by gravimetry.

Molecular weight distributions were measured by size exclusion chromatography (SEC). SEC was performed using a Waters apparatus equipped with a Waters model 510 pump, three Styragel columns in series (HR 2, HR 4, HR 6), and at 35 °C with tetrahydrofuran (THF) as eluent. The flow rate was 1.0 mL min$^{-1}$. A Waters 2410 refractive index detector was used, and molar masses were determined from a calibration curve based on PS standards.

The particle size (dp) was measured by photon correlation spectroscopy (PCS) using the unimodal analysis (Coulter N4Plus).

Liquid adsorption chromatography (LAC) was performed using a high-performance liquid chromatograph where the mobile phase used was a mixture of THF and hexane. Under these conditions PS chains eluted before PMMA chains and the block copolymers of PS/PMMA eluted between the pure polymers.

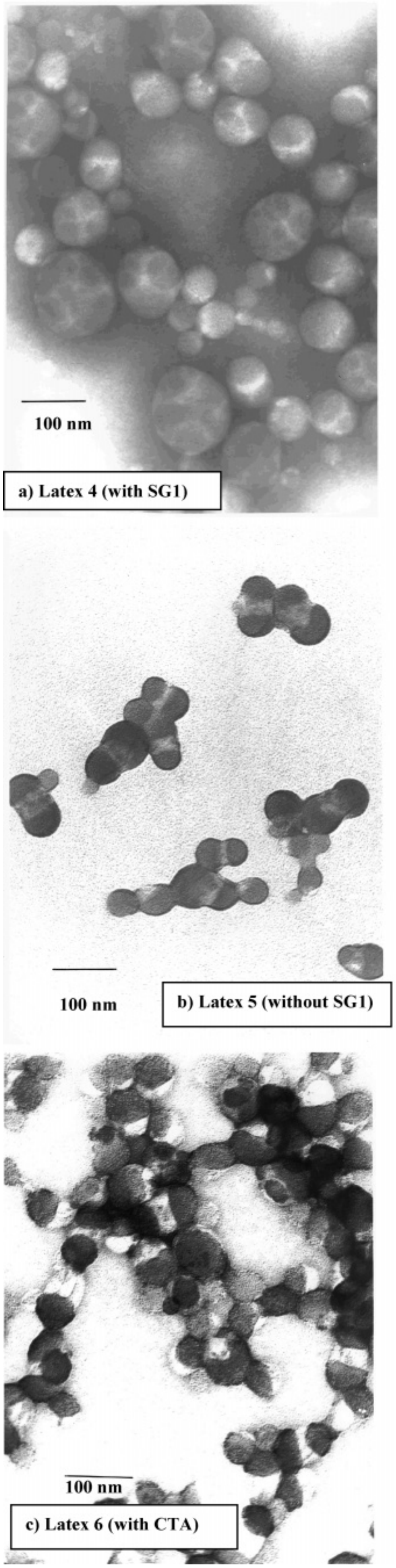


**Figure 4.** TEM micrograph of PS-*co*-PMMA composite particles stained with PTA and RuO$_4$.

The morphology of latex particles was studied by means of a transmission electron microscope, TEM (Hitachi 7000 at 75 kV). The images were taken at ×80 000 magnification. The original

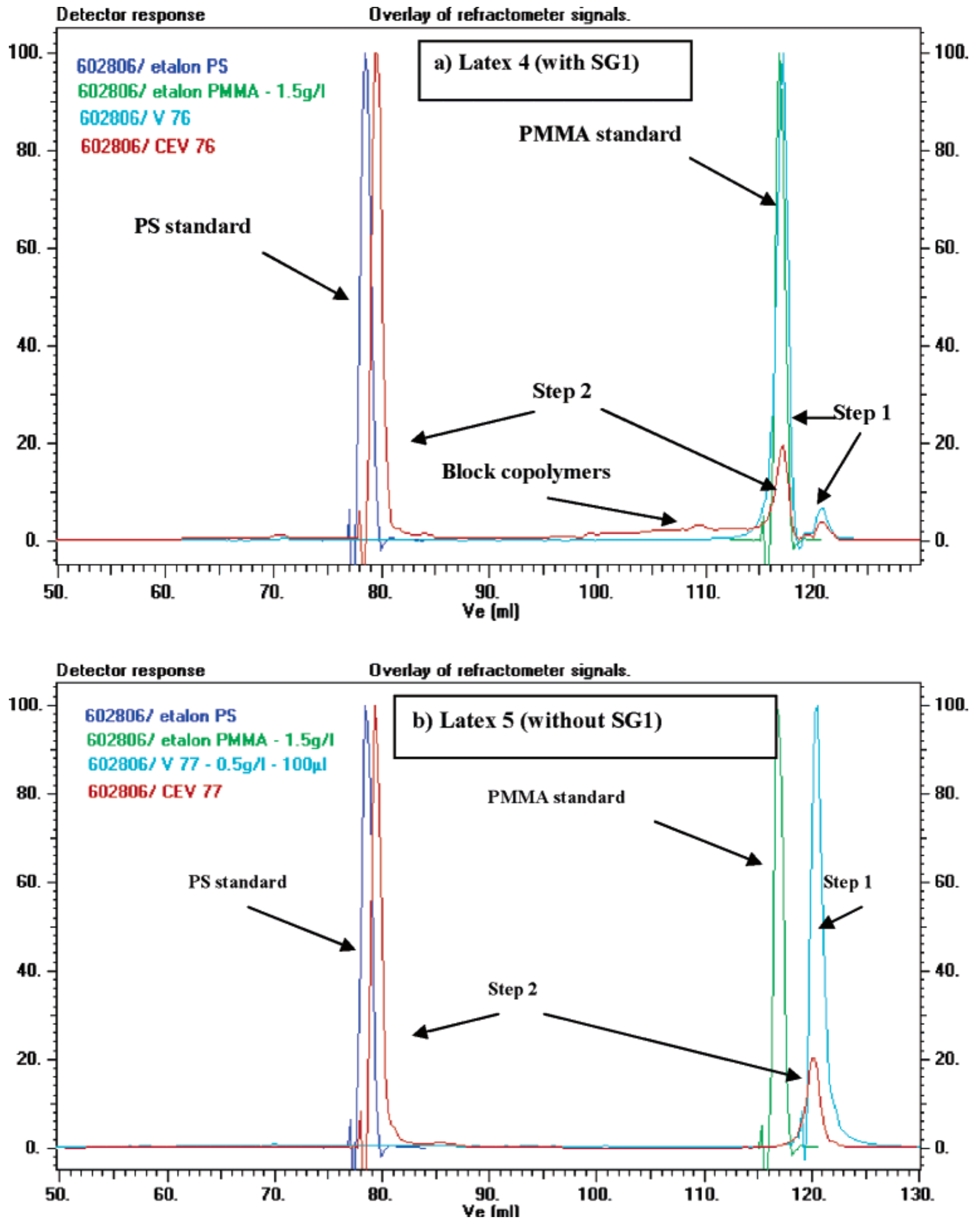


**Figure 5.** Liquid adsorption chromatograms for latexes 4 and 5 after step 1 and step 2 (see Table 3): (a) latex 4; (b) latex 5.

**Table 4. Number- and Weight-Average Molecular Weights ($\overline{M}_n$ and $\overline{M}_w$) of the Seeds Used To Prepare Latexes 1−6**

| seed | $\overline{M}_n$ (g/mol) | $\overline{M}_w$ (g/mol) |
|---|---|---|
| latex 1 (with SG1) | $3.3 \times 10^4$ | $1.2 \times 10^5$ |
| latex 2 (without SG1) | $1.8 \times 10^5$ | $5.7 \times 10^5$ |
| latex 3 (with CTA) | $1.6 \times 10^4$ | $1.2 \times 10^5$ |
| latex 4 (with SG1) | $1.8 \times 10^4$ | $9 \times 10^5$ |
| latex 5 (without SG1) | $3.1 \times 10^5$ | $4.2 \times 10^6$ |
| latex 6 (with CTA) | $2 \times 10^4$ | $1.2 \times 10^5$ |

latexes were diluted with a 0.5% aqueous solution of phosphotungstic acid (PTA) stain. A drop of each dilute latex was placed on a carbon-coated Formvar film deposited on an copper grid. Then, the samples were stained by the ruthenium tetroxide ($RuO_4$) vapor for 1 h. This allows to differentiate between PS and PMMA domains in the micrographs (PS appears dark whereas PMMA appears light).

## Results and Discussion

Figure 2 presents the TEM micrographs of latexes 1, 2, and 3. It can be seen that latex 1 presented an inverted core−shell morphology (the second stage polymer, PS, was in the center of the polymer particles). The inverted core−shell morphology is one of the equilibrium morphologies shown in Figure 1 and corresponds to a situation in which $\sigma_{12}/\sigma_{23} < 1$ and $|\sigma_{23} - \sigma_{12}|/\sigma_{13} > 1$. $\sigma_{12}$ was very small because of the presence of block copolymer as well as the formation of random poly(S-*co*-MMA) copolymer due to the incomplete conversion of MMA during stage 1. On the other hand, $\sigma_{23}$ was large because a styrene-rich copolymer was produced during the second stage using AIBN (which did not provide any hydrophilicity to the p(S-MMA)) as initiator. In addition, $\sigma_{13}$ was substantially lower than $\sigma_{23}$ because PMMA is more hydrophilic. An additional factor that made $\sigma_{23}$ greater that $\sigma_{13}$ is that KPS was used for the polymerization of MMA whereas the polymerization of S was initiated with AIBN. The sulfate moieties attached to PMMA further reduced the value of $\sigma_{13}$.

The fact that latex 1 reached the equilibrium morphology means that phase migration was not hindered by the viscosity of the PMMA matrix. This might be due to the relatively low molecular weight of the PMMA (Figure 3) and to the fact that the polymerization of styrene was carried out in batch, namely, with the polymer particles swollen with monomer.

A hemisphere morphology was obtained for latex 2. This is another of the equilibrium morphologies presented in Figure 1, and it suggests that there were important variations in the interfacial tensions with respect to latex 1. However, the seed used in the preparation of latex 2 had a molecular weight substantially higher than that of the seed of latex 1 (Figure 3). Therefore, it may be argued that the morphology of latex 2 is not the equilibrium morphology and that the differences were due to the slow migration of the PS clusters due to the high viscosity of the PMMA matrix. Nevertheless, latex 3, whose seed had a molecular weight similar to that of latex 1, also presented a hemisphere morphology. Consequently, the particle morphology of latex 1 was different because of the presence of the block copolymer that reduced the interfacial tension between the two polymers. The effect of the block copolymer on the particle morphology may be analyzed with the help of Figure 1. Let assume that point A in Figure 1 represents latex 1 because as discussed above $\sigma_{12}/\sigma_{23} < 1$ and $|\sigma_{23} - \sigma_{12}|/\sigma_{13} > 1$. In latexes 2 and 3 there were no block copolymers; therefore, $\sigma_{12}$ was larger than for latex 1. Consequently, $|\sigma_{23} - \sigma_{12}|/\sigma_{13}$ decreased and $(\sigma_{12}/\sigma_{23})$ increased, yielding a representative point (B) that was within the area in which the equilibrium morphology is hemisphere.

Figure 4a shows the particle morphology of latex 4. In the preparation of the seed of this latex, SG1 was added when the conversion was about 15%. In this latex, both PS homopolymer and PS−PMMA block copolymer was formed in the second stage. Comparison with the morphologies of latexes 5 and 6 (Figure 4, b and c, respectively) shows that particle morphology was substantially modified by the formation of the block copolymer. Latex 4 presented many polystyrene aggregates dispersed within the PMMA matrix, whereas latexes 5 and 6 presented a complete phase separation. The existence of the block copolymer in latex 4 is clearly observed in the liquid adsorption chromatograms (Figure 5). The differences between latex 4 and latexes 5 and 6 can be explained with the same arguments than used above to discuss the differences between latex 1 and latexes 2 and 3. On the other hand, the morphology of the seed of latex 4 was substantially different from that of latex 1 (Figure 2a). In the synthesis of the seed of latex 4 a nonionic initiator (AIBN) was used whereas an ionic initiator ($KPS/Na_2S_2O_5$) was used in the preparation of the seed of latex 1. Therefore, the interfacial tension polymer−water ($\sigma_{13}$) of latex 4 was likely higher than that of latex 1. The comparison of the $\sigma_{12}$ values for latexes 1 and 4 is not simple because the higher concentration of SG1 used in the preparation of latex 4, which yielded a higher amount of block copolymer, might be compensated by the random (PS−MMA) copolymer produced in latex 1. On the other hand, $\sigma_{23,\text{latex 4}}$ was likely higher than $\sigma_{23,\text{latex 1}}$ because pure polystyrene was produced in the second stage. Therefore, the representative point of the equilibrium morphology of latex 4 would be around point C in Figure 1, namely an inverted core−shell morphology. The fact that latex 4 did not attain the equilibrium morphology was likely due to the higher viscosity of the PMMA matrix as compared to latex 1, which hindered the migration of the PS clusters. The higher viscosity was a consequence of the higher molecular weight (Table 4). Similarly, latexes 5 and 6 did not reach completely the equilibrium hemispherical morphology. Thus, in latex 5 most of the particles do not have hemispherical morphology, whereas in latex 6 the number of particles with the equilibrium morphology is higher, likely because of the lower molecular weight of the seed (see Table 4).

## Conclusions

In the foregoing, a two-stage strategy for the modification of the particle morphology using block copolymers produced in situ by controlled radical polymerization was presented. It was demonstrated that the in-situ formation of a small amount of block copolymer was an effective way to improve polymer−polymer compatibility and therefore to produce new particle morphologies. The presence of the block copolymer reduced the polymer−polymer interfacial tensions modifying the surface energy of the system and hence the equilibrium morphology. It was found that equilibrium morphology was only achieved when the viscosity of the seed was low enough. Otherwise, the final morphology did not reach the equilibrium morphology. Nevertheless, even under these circumstances the final morphology was strongly affected by the presence of the block copolymer. In this work *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, SG1, was used as CRP agent, but other CRP techniques (RAFT and ATRP) can also be used.

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