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Secondary particle formation in seeded suspension polymerization

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ABSTRACT

Seeded suspension polymerization can be applied to obtain core–shell particles with particle diameters larger than 1000 μm, which finds application in the rigid foam industry, for instance. However, depending on the operation conditions, the formation of secondary particles decreases drastically the efficiency of monomer incorporation in the seed particles. In the present work, the mechanism of secondary particles formation during seeded suspension polymerization was investigated using monomers (styrene, methyl acrylate and methyl methacrylate) and initiators (benzoyl peroxide and lauroyl peroxide) with different water solubilities and, in the case of the initiators, also different decomposition rates. Results showed that there was no seed polymer in the composition of the secondary particles but only pure polymer from the monomer feed, meaning that they were not formed by erosive breakage of the swelled seeds. The fraction of secondary particles increased when monomers with higher water solubility and initiators with decreasing water solubility were used. These results were consistent with the formation of secondary particles by homogeneous nucleation and monomer droplet nucleation.

1. Introduction

Suspension polymerization is employed in the production of several important commercial resins including expandable polystyrene (EPS) foams for thermal insulation and in the packaging sector. The range of applications of these foams would be enlarged by improving the properties of EPS rigid foams, in particular their chemical resistance. Core–shell morphology is of particular interest as they can improve the chemical resistance of the foam because a shell composed by a polymer more resistant than polystyrene to organic solvents could improve the resistance of the entire foam sheet. Seeded suspension polymerization is a promising way to produce these core–shell micron-size particles provided that secondary nucleation is avoided.

Seeded polymerizations are quite common in emulsion polymerization systems in order to control particle size distribution or to produce particles with complex morphologies. According to Nomura et al. [1], one of the most important issues in semi-batch seeded emulsion polymerization is how to control secondary particle formation. When obtaining particles with core–shell structure, secondary particle formation can lead to loss of control of particle morphology, therefore a prerequisite for the formation of structured latex particles is avoidance or minimization of new particle formation when a second monomer is polymerized in the presence of a seed latex [2]. Understanding the mechanisms involved in secondary particle formation in seeded emulsion polymerization has been the subject of several works in the literature [3–5] in order to determine the conditions in which secondary nucleation could be avoided.

Despite all the extensive work on seeded emulsion polymerization, literature on seeded suspension polymerization is scarce. Lenzi et al. [6] used a semi-batch emulsion/suspension polymerization hybrid system to obtain particles formed by a suspension-like core and a shell composed by aggregated emulsion particles. The moment at which the emulsion feed was started affected the formation of secondary particles by emulsion polymerization. As a high amount of surfactant was added to the system, micellar nucleation was the main mechanism of secondary particle formation. However, the polymerization strategy was designed to favor secondary nucleation instead of avoiding it.

Some information on the formation of secondary particles in the presence of large suspension particles can be obtained from the studies of classical suspension polymerization. In this process, particles are formed due to monomer droplet nucleation and the final particle size distribution is a result of the interplay between the breakage and the coalescence of the monomer droplets. The former mainly occurs in regions of high shear stress (i.e., near the agitator blades) or as a result of turbulent velocity and pressure variations along the surface of a drop. The latter is either increased or decreased by the turbulent flow [7]. The balance

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between breakage and coalescence is controlled by a number of factors [7–12] including the viscosity and density of the continuous and dispersed phases. According to Kotoulas and Kiparissides [13], when drop breakage occurs by viscous shear forces, the monomer droplet is first elongated into two fluid lumps separated by a liquid thread. Subsequently, the deformed monomer droplet breaks into two almost equal size drops, corresponding to the fluid lumps, and a series of smaller droplets corresponding to the liquid thread, in a process known as thorough breakage. On the other hand, drop breakage can also occur by erosive breakage, in which a droplet suspended in a turbulent flow field becomes marginally unstable and then a number of small droplets are stripped out from the initial one. At the later stages of polymerization, droplets become rigid polymer particles due to the high polymer fraction. This is called Particle Identification Point (PIP) as it defines the moment in which no breakage or coalescence takes place [14]. Kalfas et al. [5] discussed the formation of emulsion particles during classical suspension polymerization using monomers with different water solubilities concluding that the formation of emulsion particles by homogenous nucleation depended on the water solubility of monomer. Polymer formed in the emulsion particles presented higher molecular weight than the polymer formed in the suspension particles due to the segregation of radicals in the emulsion particles. Ma and Li [4] also observed the formation of secondary particles when studying the synthesis of monodisperse polystyrene particles with diameters about 5–10 μm by microsuspension polymerization employing the microporous membrane method. Surfactant was added to the system (at concentration below the critical micellar concentration) in order to avoid coalescence. Although the stirring rate used was not reported, one would expect that a relatively low agitation speed was applied because it was intended to obtain monodisperse particles. Therefore the formation of secondary particles by shear induced breakage of the micron-sized monomer droplets [15,16] was unlikely. The authors concluded that the secondary particles were formed by homogeneous nucleation.

These works showed that homogeneous nucleation takes a very important role on secondary particle formation during batch suspension polymerization. Nevertheless, semi-batch seeded suspension polymerization systems present unique characteristics (such as the monomer feed flow rate and the mass transfer mechanisms of monomer to the polymer particles) that greatly differ from classical suspension polymerization. In order to efficiently produce structured particles through seeded suspension polymerization, secondary particle formation should be avoided, therefore it is of key importance to understand the mechanisms involved in its formation. In the present work, the formation of secondary particles in a seeded suspension polymerization system is discussed. Polystyrene particles with diameters about 1 mm were used as seeds and experiments were carried out using initiators and monomers with different water solubilities. Based on the gathered information, the mechanisms involved in secondary particle formation are discussed.

2. Experimental section

2.1. Materials

Technical grade styrene, methyl methacrylate (MMA) and methyl acrylate (MA) were used as shell-monomers. Benzoyl peroxide (BPO, Sigma–Aldrich, 98% purity) and lauroyl peroxide (LPO, Sigma–Aldrich, 98% purity) were used as initiators. Distilled water was used as suspending medium and poly(vinyl pyrrolidone) (PVP, 360,000 g/mol, Technical grade, Sulpolímeros) as stabilizer. Ascorbic acid (Sigma–Aldrich, 99% purity) was used to avoid inhibition caused by oxygen. All chemicals were used as-received without purification.

Polystyrene seeds were obtained by batch suspension polymerization at 90 °C, using BPO as initiator ($0.0023\ \mathrm{g/g_{sty}}$) and PVP as stabilizer ($0.01\ \mathrm{g/g_{water}}$). Polymer beads were washed, dried and the particles retained between the sieves with an aperture of 710 and 1180 μm were used as seeds (an average diameter of 945 μm).

2.2. Seeded suspension polymerization

Seeded suspension polymerization experiments were carried out in a 1-L jacketed reactor; the formulation used in all reactions is presented in Table 1. The initial charge consisted in polystyrene seeds, distilled water, poly(vinyl pyrrolidone) and ascorbic acid. The reaction medium was heated to 50 °C after the addition of the initial charge to the reactor. The solution of monomer and initiator was then added under vigorous stirring (900 rpm) at 0.9 g/s. As soon as the monomer feed finished, temperature was increased to 70 °C and the system was allowed to react for 4 h. The reaction temperature profile is illustrated in Fig. 1. Initiators (benzoyl peroxide – BPO, and lauroyl peroxide – LPO) were used at the concentration of 0.23 mol%. The fraction of monomer used (in relation to the total organic phase) was low in order to keep polymer concentration in the seed particles above the particle identification point. In the case of polystyrene, the PIP is considered to be around 70% of polymer concentration. This precaution was adopted in order to avoid turbulent breakage of the seed particles when swelled by the monomer.

2.3. Standard batch suspension polymerization

Batch methyl methacrylate suspension polymerization was carried out in order to compare the polymer molecular weight with that of the core–shell particles. The formulation was the same as described in Table 1, but without the polystyrene seed. Water, ascorbic acid, poly(vinyl pyrrolidone) were added to the reactor; meanwhile, initiator (benzoyl peroxide, 0.341 g) was dissolved in methyl methacrylate. The system was heated to 50 °C and the monomer/initiator solution was added to the reactor. Temperature was increased to 70 °C and stirring rate was set to 900 rpm; the system was allowed to react for 4 h.

2.4. Characterization

Particle composition was determined by ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR); the particles were dissolved in deuterated chloroform, $CDCl_3$; the spectra were recorded at 20 °C using a Bruker Advance spectrometer (500 MHz). The molar percentage of monomer incorporated to the particles was determined using the peak of CH_3–O group (at 3.6 ppm), and the peaks correlated to the aromatic ring (between 7.2 and 6.2 ppm). The peaks correlated to the CH_2 and CH groups were used to verify the integration error. The fraction of secondary particles formed in the cases in which MMA and MA were used as shell-monomers was calculated using Equation (1). In the case of styrene as shell-monomer,

Table 1
Formulation used for core–shell synthesis.

Reagent	Mass (g)
Water	560.00
Polystyrene seed	197.40
Monomer	62.00
BPO/LPO	0.341/0.561
Poly(vinyl pyrrolidone)	1.980
Ascorbic acid	0.789

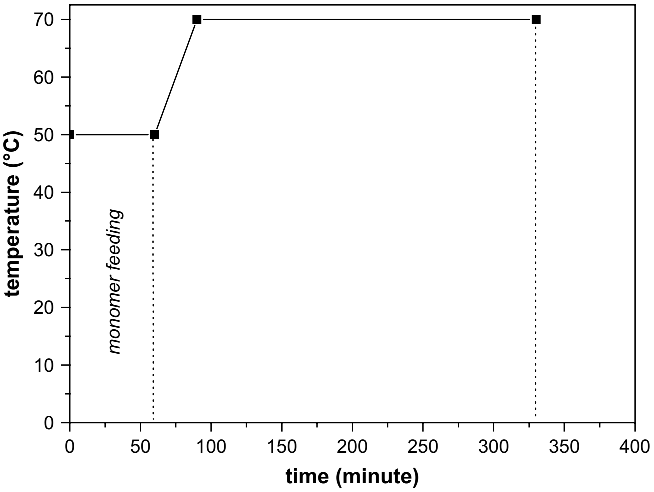


Fig. 1. Temperature profile used in the core–shell synthesis.

efficiency of incorporation was calculated by gravimetry using the separation procedure described in Fig. 2.

$$\%_{\text{secondary particles}} = \left(1 - \frac{\text{monomer incorporated}}{\text{monomer added}}\right) \times 100 \quad (1)$$

Scanning Electron Microscopy (SEM, Philips XL-30) was used to evaluate the core–shell particle surface and the morphology of the secondary particles; images were obtained at 15 kV from gold coated samples. The morphology of latex particles was also studied by means of Transmission Electron Microscopy (TEM, Hitachi 7000) at 75 kV. The images were taken at 30,000 and 60,000 magnification. The original 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 a copper grid.

Molecular weight distributions were measured by Size Exclusion Chromatography (SEC). It was performed using a Waters apparatus equipped with three Styragel columns in series (HR 2, HR 4, HR 6; effective molecular weight ranges of 5×10^2–2×10^4, 5×10^3–6×10^5 and 2×10^5–1×10^7, respectively) and at 35 °C with tetrahydrofuran (THF) as eluent (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 (average molecular weights varying from 580 to 11,200,000 g/mol).

2.5. Separation of the secondary particles from primary particles

Due to the difference of sizes between primary (seed particles after the seeded suspension polymerization reaction) and secondary particles, the former can be easily separated from the others by simple sedimentation. The irregular agglomerates were separated from the aqueous phase by centrifugation: water phase was centrifuged until no particles were detected by optical microscopy at 10× magnification; centrifugation at 1000 rpm for 12 min was enough to assure an efficient separation. The residual aqueous phase was obtained after centrifugation and the residue was evaluated by Scanning Electron Microscopy and Transmission Electron Microscopy. Primary particles and agglomerated secondary particles were also evaluated by Scanning Electron Microscopy. A diagram of the separation scheme is presented in Fig. 2.

2.6. Separation of PMMA from polystyrene in the primary particles

PMMA was separated from PS before SEC analysis. A sample of the primary particles was dissolved in THF; after complete dissolution, cyclohexane was slowly added until PMMA precipitation occurred. The precipitate was separated by sedimentation and dried; after, it was dissolved in acetic acid to separate any trace of polystyrene. Acetic acid soluble fraction was filtered and dried; infrared spectra (Nicolet 5DXC FTIR spectrometer) were obtained from the PMMA and PS fractions, confirming that they are composed of pure polymer (peaks at 700 and 750 cm^{-1} were used to identify the presence of polystyrene, while the peak at 1740 cm^{-1} was used for PMMA). A diagram of the separation scheme is presented in Fig. 3.

3. Results and discussion

3.1. Particle morphology and composition

The separation procedure of the particles described above was implemented yielding three distinct fractions: core–shell particles, “agglomerate-like” particles (sizes from a few micrometers to 1 mm) and the aqueous phase. One drop of the aqueous phase was deposited on a copper grid to be evaluated by TEM, demonstrating the presence of secondary submicron particles (Fig. 4 below). Fig. 5 presents SEM images of the agglomerates. The ^{1}H NMR spectra of the submicron particles and the agglomerates are presented in Figs. 6 and 7, respectively.

TEM and SEM images showed the presence of particles with an average size of 300 nm in the aqueous phase, which explains the changes of the water phase from transparent to opaque. These submicron particles formed the agglomerates of irregular shape with sizes from a few micrometers to 1 mm (Fig. 5). In all the cases the weight fraction of agglomerates was much higher than the

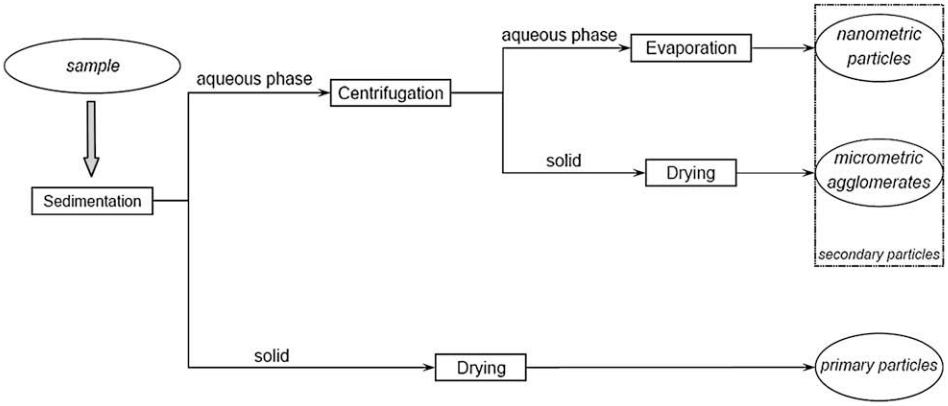


Fig. 2. Separation of primary and secondary particles.

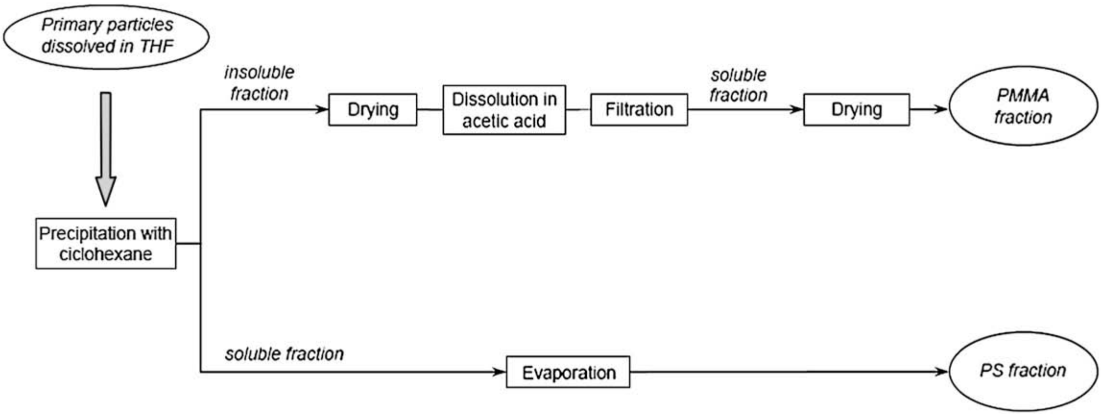


Fig. 3. Separation of the PMMA from the primary particles.

fraction of submicron particles. Actually, only less than 2 wt% of the total of secondary particles was found as submicron particles.

The composition of both submicron particles and agglomerates was evaluated by ^{1}H NMR. However, impurities must be removed before analysis (PVP or any trace of the other chemicals as BPO or ascorbic acid). In the case of agglomerates, it was accomplished by dissolving them in tetrahydrofuran (THF); the insoluble fraction was separated by precipitation and the soluble fraction was dried and used to prepare the NMR sample. In the case of the submicron particles, aqueous phase was evaporated and the solid fraction was mixed in THF. Again, insoluble fraction was separated by precipitation and the soluble fraction was dried and used to prepare the NMR sample. Spectra are presented in Figs. 6 and 7. These figures demonstrated that the agglomerates and the submicron particles were composed only by PMMA because of the presence of peaks at 0.8 and 1.3 ppm (characteristic of C–CH_3 group) and 3.6 ppm (characteristic of O–CH_3 group) and because there were no peaks at the region characteristic of polystyrene aromatic ring (between 7.2 and 6.2 ppm).

The formation of the agglomerates can be explained by the fact that no surfactant was added to the system and the amount of PVP employed was not enough to guarantee the stabilization of the large surface area generated by the nucleation of submicron particles during the reaction. Therefore, as the submicron particles were formed, most of them coagulated. These newly formed agglomerates continued to coagulate with submicron particles and other agglomerates until sizes large enough to be stabilized by the suspension stabilizer (PVP) were reached.

The small diameters of the secondary particles suggest that they could not be formed through a conventional suspension polymerization mechanism. Suspension polymerization systems generate particles in the micrometric scale, i.e., at least 2 orders of magnitude larger than the submicron particles produced here [10–18]. In addition, they could not be formed by the erosion of the monomer swelled seed particles, since there was no polystyrene in their composition.

Taking into account the results presented above, the formation of secondary particles was investigated by using monomers and initiators of different water solubilities.

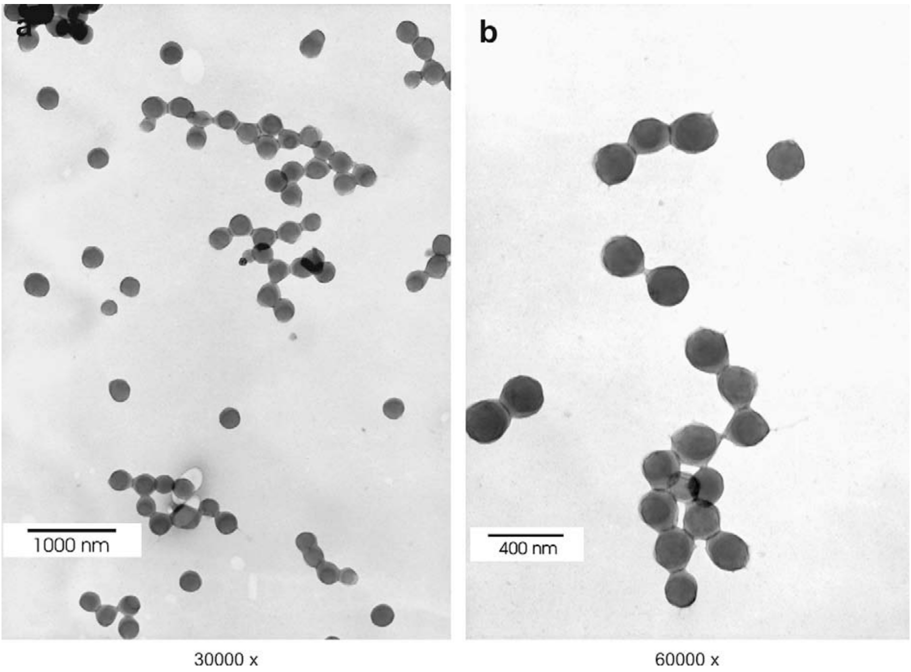


Fig. 4. TEM images of the secondary particles. (a) 30,000×; (b) 60,000×.

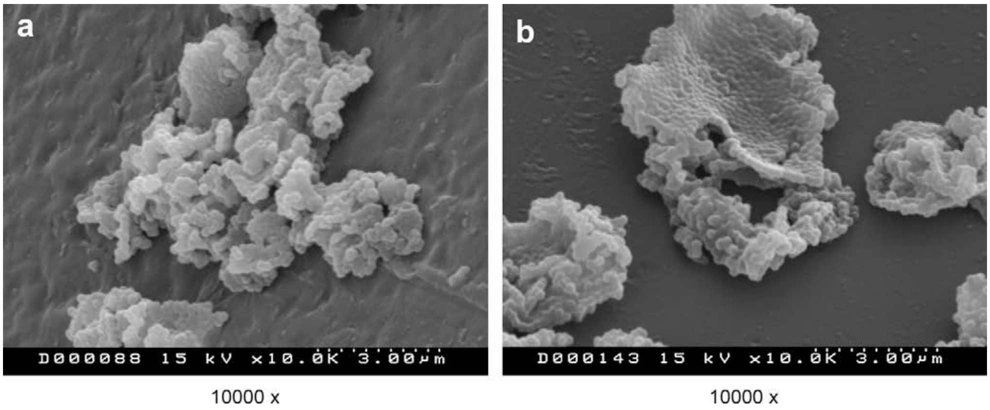


Fig. 5. SEM images of the agglomerated particles. (a) 10,000×; (b) 10,000×.

3.2. *Secondary particle formation – influence of monomers and initiators*

Experiments were carried out using the same reaction procedure as described above. Styrene, methyl methacrylate and methyl acrylate were used to prepare the shell. Their respective water solubilities are presented in Table 2. Table 3 presents the fraction of secondary particles formed, calculated by the molar relation of monomer incorporated in the primary particles and the monomer added to the system (Equation (1)). The initiator used was BPO at 0.23 mol%.

It may be observed that the type of monomer strongly influenced the formation of secondary particles. Although many factors are known to influence the secondary particle formation in dispersed polymerization systems (such as the type and concentration of the surfactant, monomer feed rate in semi-batch systems, stirring rate, viscosity,…) the increase in the fraction of secondary particles formed is closely related to the type of monomer employed since all other experimental conditions were kept constant and the main difference between the monomers is their water solubility. Styrene, which is rather water insoluble, was almost totally incorporated in the seeds, while a large fraction of MMA and methyl acrylate polymerized outside the seed particles. The results obtained with MMA and MA are at first sight surprising, because considering the particle/water partition coefficients of these monomers ($K_{MMA} = 38$; $K_{MA} = 11$) under equilibrium conditions, only 7% of MMA and 19% of MA were in the aqueous phase, the rest being in the seed particles. In addition, a rather water insoluble initiator (BPO) was used in these experiments, which under thermodynamic equilibrium conditions should be mostly in the organic phase. This would result in a much lower fraction of secondary particles. Therefore, the system could not be under

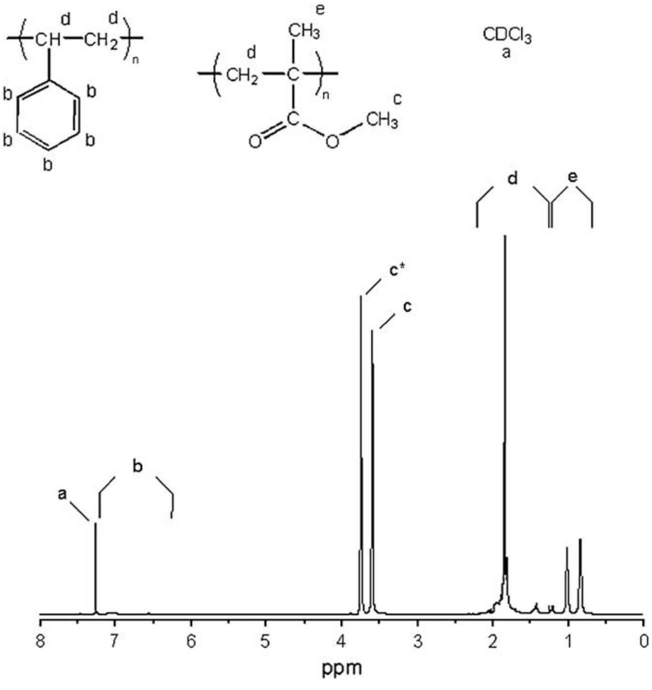


Fig. 6. ^{1}H NMR spectrum of the agglomerates.

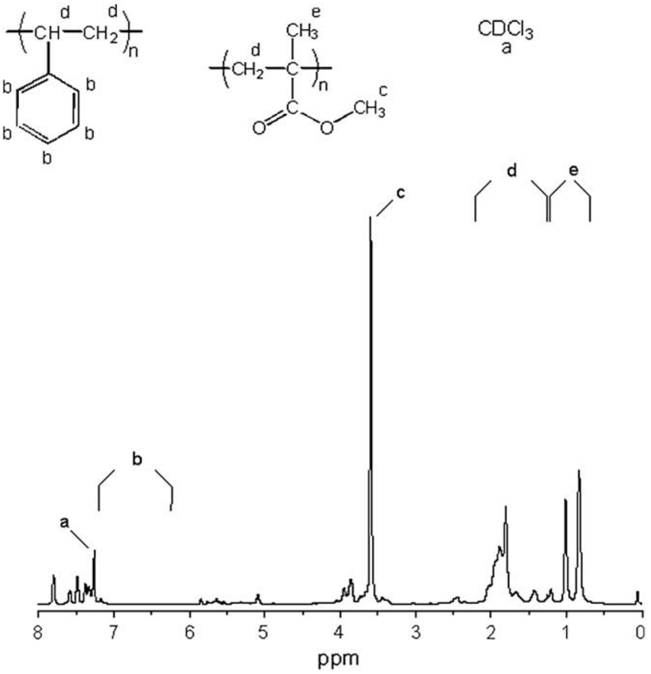


Fig. 7. ^{1}H NMR spectrum of the submicron particles.

Table 2
Monomer water solubility.

Monomer	Water solubility (g/100 g_{H_2O})	Reference
Styrene	0.0271 (25 °C)	Zhang and Ray [19]
Methyl methacrylate	1.59 (20 °C)	Min and Ray [20]
Methyl acrylate	5.2 (20 °C)	Min and Ray [20]

Table 3
Distribution of the second stage monomer between the secondary and core–shell particles.

Monomer	Fraction in secondary particles (%)
Styrene	3
Methyl methacrylate	60
Methyl acrylate	88

Table 4
Water solubility and half-life times of the initiators used and distribution of the second stage monomer between the secondary and core–shell particles.

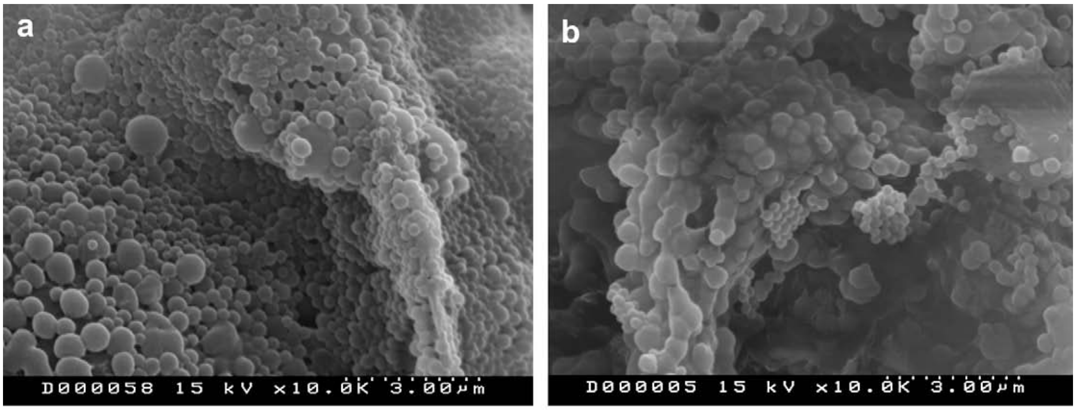
	Water solubility [21] ($g/100\ g_{water}$)	Half-life time [22] (hours at 75 °C)	Fraction in the secondary particles	
			Styrene	MMA
BPO	3×10^{-4}	10.5	3	60
LPO	2×10^{-9}	1.9	16	78

thermodynamic equilibrium conditions, namely, the process was mass transfer limited.

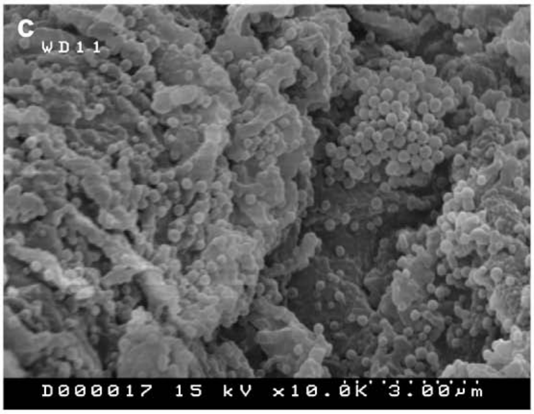
A mechanism that may explain these results is as follows. A fine dispersion of monomer droplets containing the initiator was fed into a reactor containing a dispersion of polystyrene suspension particles. Monomers could diffuse relatively fast to the seed particles but diffusion within the hard seed particles may be slow. The initiator, which is rather water insoluble, diffused slowly to the aqueous phase and then to the polymer particles. Some of the initiators decomposed in the aqueous phase forming radicals. These radicals may react with the monomer dissolved in the aqueous phase. Because of its low water solubility this was not a likely process for styrene, but the likelihood substantially increased for MMA and even more for MA. The oligoradicals formed precipitated when they reached a critical length, and the precipitated polymer was stabilized by the poly(vinyl pyrrolidone) present in the reactor, forming secondary particles. These particles correspond to the so-called submicron particles. According to this mechanism, it is expected that the number of secondary particles increased with the water solubility on the monomer, i.e., with the likelihood of occurrence of polymerization in the aqueous phase. From the instant of their formation, newly formed particles were plasticized by absorbed monomer, therefore no limitations to the monomer mass transfer within the secondary particles occurred and polymerization was relatively fast in these particles. Another factor that may accelerate the polymerization rate in the secondary particles as compared with the seed particles was radical compartmentalization. Poly(vinyl pyrrolidone) is a polymeric surfactant that does not diffuse fast through the aqueous phase and hence it is not efficient in stabilizing newly formed particles. Therefore, massive coagulation of the submicron particles occurred yielding micrometer aggregates.

Experiments were carried out using benzoyl peroxide and lauroyl peroxide as initiators and MMA and styrene as monomers. Table 4 presents water solubility values, half-life data for the initiators and the fraction of shell polymer formed in each case. Fig. 8 presents SEM images of the agglomerated secondary particles formed in the systems MMA/BPO, MMA/LPO and Styrene/LPO.

An additional process that may lead to the formation of secondary particles is the polymerization in the entering droplets. It has been demonstrated that LPO can stabilize droplets against



Styrene/LPO (0.23 mol%). MMA/LPO (0.23 mol%).



MMA/BPO (0.23 mol%).

Fig. 8. SEM images of the secondary particles formed during core–shell synthesis (10000×). (a) Styrene/LPO (0.23 mol%); (b) MMA/LPO (0.23 mol%); (c) MMA/BPO (0.23 mol%).

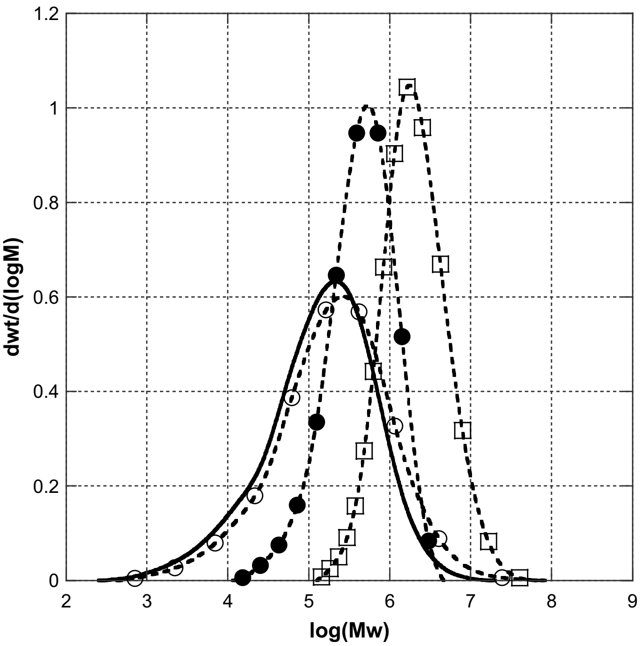


Fig. 9. MWDs of the PMMA obtained in the (–□–) core–shell particles, (–○–) agglomerates and (—) submicron particles and (–●–) in batch suspension polymerization (BPO concentration of 0.23 mol%; 70 °C).

Oswald ripening, namely acting as costabilizers in miniemulsion polymerization [21]. However, the results obtained with styrene show that this process was not the major one when BPO was used.

The faster rate of radical formation of LPO as compared with BPO enhanced droplet nucleation. The fact that, as shown in Fig. 8, the average size of the submicron particles was larger for LPO than for BPO (300 nm for MMA/BPO; 300–1000 nm for MMA/LPO; 600–1000 nm for S/LPO) which supports the idea that droplet nucleation gained importance for LPO.

Fig. 9 presents the molecular weight distributions for the PMMA formed as secondary particles (both agglomerated and submicron particles) as well as the PMMA formed inside the seed particles (MMA as shell-monomer, BPO concentration of 0.23 mol%, 70 °C). For the sake of comparison, MWDs of the PMMA obtained in standard batch suspension polymerization (70 °C, 0.23 mol%) are also included in Fig. 9.

Fig. 9 shows that the molecular weights produced in the seed particles were substantially higher than those produced in either the submicron particles/aggregates or in conventional suspension polymerization. This clearly indicated that the polymerization in the seed particles was affected by a strong gel effect that reduced the termination rate resulting in the increase in molecular weights. This strongly supports the hypothesis that the monomer transfer was diffusionally controlled within the seed particles. On the other hand, the secondary particles presented lower molecular weights and higher Polydispersity Indexes than the PMMA obtained by batch and seeded suspension polymerizations. The low values of molecular weights indicate that the radical concentration inside the secondary particles was high, suggesting that the monomer concentration in these nanoparticles/agglomerates was given by thermodynamic equilibrium.

4. Conclusions

The formation of secondary particles during seeded suspension polymerization was investigated. Images from Scanning Electron Microscopy and Transmission Electron Microscopy demonstrated that these secondary particles, presenting diameters of a few hundred nanometers, are dispersed in the water phase or are present as micrometric, irregular agglomerates, since no surfactant was added to the system in order to stabilize them.

Nuclear Magnetic Resonance did not detect the presence of polystyrene in the secondary particles, indicating that they were not formed by erosive breakage of the swollen primary particles. The fraction of secondary particles formed increased when monomers with higher water solubility were used. The formation of secondary particles also increased with lauroyl peroxide (LPO) as compared to benzoyl peroxide (BPO), In addition, monodisperse secondary particles were obtained with BPO and polydisperse particles when LPO was used. These results were in agreement with a mechanism in which secondary particles were formed mainly by homogeneous nucleation in the case of BPO. When a more hydrophobic initiator was employed, LPO, not only homogeneous nucleation took place, but also the nucleation of the monomer droplets which was responsible for the formation of secondary particles.

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