PARTICLE NUCLEATION USING DIFFERENT INITIATORS IN THE MINIEMULSION POLYMERIZATION OF STYRENE

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Abstract - In miniemulsion polymerization, droplet nucleation is the key factor to ensure the production of polymer particles with a desired composition. The influence of the initiation on droplet nucleation is conflicting and it has not been completely considered. The result of employing different initiator systems on the nucleation mechanism and kinetics in the polymerization of stable styrene/polystyrene miniemulsions with varied droplet size is discussed here. The initiation systems employed provide all combinations between the phase (aqueous or organic) where initiation mainly occurs and the phase affinity of the produced radicals. Latexes with different contributions of droplet nucleation were synthesized according to the employed initiation system and the droplet size of the miniemulsion. The results presented here could be used as a guide for choosing the initiation system to achieve the required contribution of droplet nucleation.
Keywords: Miniemulsion polymerization; Particle nucleation; Polystyrene.

INTRODUCTION

Miniemulsion (ME) polymerization represents an alternative for the synthesis of hybrid latexes and enables the incorporation of a hydrophobic component into the polymer particles without requiring its diffusion through the aqueous phase [Asua 2002; El Aasser and Miller 1997; Sudol and El Aasser 1997; Schork et al., 1999]. In fact, in a ME polymerization the nucleation is carried out in previously stabilized submicron droplets (50 - 500 nm), which contain all the components that are desired to incorporate into the material. Therefore, the final properties of a latex synthesized by ME polymerization are mainly determined by the droplet nucleation. Although it is accepted that droplet nucleation is affected by the ME stability, droplet size, and the amount of free surfactant in the aqueous phase, the initiation (radical formation) is an important parameter that has not always been considered.

Both water-soluble and oil-soluble initiators were employed in ME polymerization. Although the former is the most frequently employed, there is an increasing use of oil-soluble initiators. Experimental evidence about the influence of initiation systems in ME polymerization is conflicting and most of the works focus their attention on the polymerization kinetics [Luo and Schork 2002; Tsavalas et al., 2003; Autran et al., 2007; Blythe et al., 1999; Alduncin et al., 1991; Costa et al., 2013].

It was reported that ME polymerization of butyl acrylate (BA) initiated with an oil-soluble initiator (2,2'-azobisisobutyronitrile: AIBN) proceeded slower in the presence of a water-soluble radical scavenger ($NaNO_2$) than in the absence of such scavenger, and this effect was stronger for smaller polymer particles

[Luo and Schork 2002]. This was considered as an indication that the radicals formed in the aqueous phase play an important role in the polymerization. In the ME polymerization of acrylic monomers in the presence of alkyd resins, Tsavalas *et al.* (2003) observed a decrease in the methyl methacrylate (MMA) polymerization rate and the final monomer conversion from the water-soluble initiator (potassium persulfate: KPS) to the oil-soluble initiation system (AIBN or benzoyl peroxide: BPO). It was explained by a reduction in water phase concentration of the oil-phase initiators due to the consumption of a large fraction of the produced radicals in termination reactions within the droplets. Based on the results of Luo and Shork (2002) and using a polymer-particle population model, Autran *et al.* (2007) showed that radical desorption (instead of aqueous-phase radical formation) was the key mechanism in controlling the kinetics of the ME process when AIBN was used as oil-soluble initiator in the polymerization of BA. Similar results had been previously published by Alduncin *et al.* (1991) in both the seeded emulsion and the ME polymerization of styrene (St) with AIBN, where initiation mainly occurred in the oil-phase, and particles containing a single radical were principally formed by desorption of primary radicals. Also, Blythe *et al.* (1999) reported that the most likely source of radicals in ME polymerization of St with the oil-soluble initiator 2,2'-azobis(2-methyl-butyronitrile) is the oil phase. Recently, Costa *et al.* (2013) investigated experimentally and computationally the ME homopolymerization of MMA, St and BA with AIBN as initiator. For each monomer system, a limiting particle size was determined, above which the effect of compartmentalization became negligible and the polymerization kinetics did not depend on the particle size as in a bulk polymerization. It is important to remark that previous reported studies assumed that all particles were produced by droplet nucleation.

Differences in the nucleation mechanisms were reported depending on the initiators employed. Chern and Liou (1999a, 1999b) investigated the effect of the initiator type (AIBN vs. KPS) on the extent of droplet nucleation in the styrene (St) ME polymerization by using a water-insoluble dye dissolved in the monomer droplets. They found that the oil-soluble initiator promoted nucleation in the monomer droplets, whereas micelar and homogeneous nucleation predominated in the system initiated with water-soluble KPS [Chern and Liou 1999a]. Also, they observed that the higher the AIBN concentration, the higher the number of particles produced by secondary nucleation, which implies that

the fraction of AIBN dissolved in water played an important role in the particle formation process [Chern and Liou 1999b].

The incorporation of preformed polymer in miniemulsions can affect the droplet size, depending on its concentration and its molecular weight [Lopez *et al.*, 2008; Blythe *et al.*, 2000]. Colmán *et al.* (2011) investigated the effect of adding 10-20% of polystyrene (PS) and Poly(methyl methacrylate) on the kinetics and nucleation mechanism of ME homopolymerizations of St and MMA, employing KPS as initiator. They reported that the secondary nucleation mechanism is less important in the ME homopolymerization of MMA than that of St, due to the smaller initial droplet size observed in the former. Similar results were observed by Rodrígues *et al.* (2007) in the batch ME polymerization of a silicone-acrylic system employing KPS as initiator. High silicone contents yielded relatively large droplets (177 nm), and hence particle formation by homogeneous nucleation was significant.

Note that the reported effect of initiation systems on ME polymerization is a bit conflicting; not all the initiation alternatives were studied in the same ME system and with varied droplet size, and the contribution of droplet nucleation on the particle formation was not always considered. This work investigates the influence of the main variables of the initiation system on both the kinetics and the droplet nucleation in the polymerization of stable St MEs with varied droplet size. The studied initiator types provide a wide combination between the phase where initiation mainly occurs, the phase affinity of the radicals produced and the rate of initiation. The initiators employed were KPS, tert-butyl hydroperoxide/ ascorbic acid (TBHP/AsAc), tertbutylperoxy 2-ethylhexyl carbonate (TBEC), and BPO. The droplet size of the stable St MEs and the organic phase viscosity were varied with the content and molecular weight of the preformed PS dissolved in the organic phase.

EXPERIMENTAL

Materials

Demineralized water was used throughout the work. The water-soluble initiator, KPS, (Mallinckrodt, 99% purity), the organic-soluble initiators, BPO (BDH, wet with 30% water) and TBEC (Trigonox 117, AkzoNobel, 95% purity), and the water-soluble redox system TBHP/AsAc (Aldrich/Cicarelli, molar ratio 2/1) were employed. Hexadecane (HD, Merck, ≥ 99% purity) was used as costabilizer, sodium

lauryl sulphate (SLS, Cicarelli, 95% purity) as surfactant, hydroquinone (HQ, Fluka AG, > 99% purity) as polymerization inhibitor, sodium bicarbonate as buffer salt (Anedra, purity 99.7%) and isopropyl alcohol (Cicarelli) as coagulation reagent. St was washed with an aqueous solution of potassium hydroxide to remove the polymerization inhibitors, and then with demineralized water until reaching the pH of the washing water. *Iso*-octyl-3-mercaptopropionate (*i*OMP, Aldrich, isomers mixture > 99%) was used as Chain Transfer Agent (CTA) for controlling the molecular weight of preformed PS. A set of 9 narrow PS (Shodex) standards in the molar mass range 10^3-10^6 g/mol was used for calibration of the size exclusion chromatography (SEC) system. Tetrahydrofuran (HPLC Solvent, J.T. Baker) was used as eluent in the SEC runs.

Preformed PS

Three PS produced by conventional emulsion polymerization were employed as preformed polymers. These PS were added to the organic phase with the objective of achieving stable MEs with varied droplet size. PS of low molecular weight (PS_L) was synthesized under semicontinuous unseeded starved conditions, feeding a solution containing St and CTA at constant rate in order to obtain a number-average molecular weight ($\bar{M}_n$ =15000 g mol^{-1}) with low polydispersity. PS of intermediate (PS_I) and high (PS_H) molecular weights were produced under unseeded batch conditions with the recipes reported in Minari *et al*. (2008) The measured average molecular weights ($\bar{M}_n$ and $\bar{M}_w$), determined by SEC, of the preformed PS are summarized in Table 1. The three PS latexes were coagulated with isopropyl alcohol, and the remaining emulsifier was eliminated by successive cycles of centrifugation and redispersion with demineralized water until reaching the surface tension and conductivity of the washing water in the supernatant.

Table 1: Molecular weights of the preformed PS.

Nomenclature	$\bar{M}_n$ (×10^{-3} g mol^{-1})	$\bar{M}_w$ (×10^{-3} g mol^{-1})
PS_L	15.2	33.4
PS_I	54.4	380.8
PS_H	333.2	1755.0

Miniemulsification

All ME contained 20% wt solids contents, varied content of preformed PS, 2% wbop (weight based on organic phase) of SLS, 4% wbm (weight based on monomer) of HD, and NaHCO$_3$ at a concentration of 0.024 M in the water phase. The preformed PS was dissolved in the organic phase and maintained under stirring for 12 h before miniemulsification. In order to produce the miniemulsions, the organic and the aqueous phases were strongly mixed by magnetic stirring during 15 min, and the resulting preemulsion (around 200 ml) was sonified with a Sonics VC 750 equipment (power 750 watts) during 25 min, at 100% of amplitude with cycles of 20 seconds on and 5 off. During sonication, miniemulsions were magnetically stirred and their temperature was maintained below 30 ºC by means of an ice bath.

Polymerization

Polymerizations were carried out in batch in a 0.3 L jacketed glass reactor equipped with reflux condenser, stirrer, sampling device, and nitrogen inlet. The reaction temperature (70 or 80 ºC) was controlled by manipulating the temperature of the fluid in the jacket by means of a thermostatic bath. The miniemulsion was added to the reactor and kept under stirring and nitrogen bubbling. When the oil-soluble BPO or TBEC were used as initiators, they were dissolved in the organic phase before miniemulsification. The KPS initiator was first dissolved in water and then added into the reactor as a shot. In the experiments with TBHP/AsAc, 20% of both reactants were initially loaded to start the polymerization, and the remaining 80% were fed in separate streams at constant flow rates, during 45 min. The total polymerization time was 2 h for the reactions with KPS or TBHP/AsAc, and it was extended to 3 h when BPO or TBEC were used.

Figure 1 shows the global chemical reactions for the radical formation corresponding to each initiation system. Their main characteristics are: i) KPS produces water soluble SO$_4^-$ radicals (Figure 1 A), which must first polymerize in the water phase until becoming sufficiently hydrophobic to enter into the organic phase; ii) TBHP/AsAc is a redox initiator able to control the flux of radicals from the water phase, where the produced tert-butoxyl radicals (Figure 1 B) are hydrophobic enough to directly enter into the organic phase; iii) TBEC and BPO are oil-soluble initiators that produce hydrophobic radicals inside the monomer droplets and polymer particles (Figure 1 C and D). Although tert-butoxyl, 2-ethylhexyl carbonate and benzoyloxyl radicals are hydrophobic, they have different affinities for the aqueous phase, with the following increasing hydrophobicity sequence: tert-butoxyl < benzoyloxyl < 2-ethylhexyl carbonate.
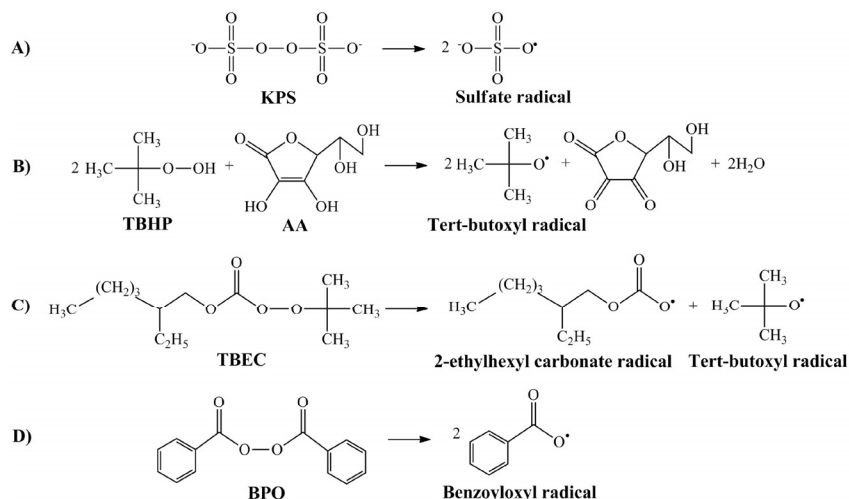
Figure 1: Radical formation reactions for the different initiation systems employed.

Characterization

The ME surface tension (γ) was measured with a Krüss K8tensiometer. Stability of MEs was analyzed by scanning the backscattering along the height of a vial every 5 min and for 4 h with a Turbiscan TMA2000. The evolution of the backscattering signal during the measurement time gives an indication of the ME stability, where a smaller change in the backscattering signal indicates a more stable ME.

The following were measured on samples withdrawn during the reactions: i) monomer conversion (x), by gravimetry; ii) average droplet diameter (d_d) and particle diameter (d_p) by dynamic light scattering (DLS) at a detection angle of 90º, in a Brookhaven BI-9000 AT photometer; iii) intensity based droplet and particle size distributions by numerical inversion of the DLS autocorrelation measurements [Clementi et al., 2010]; and iv) volume particle size distribution (PSD) by capillary hydrodynamic fractionation (CHDF), with a Model 2000 Matec Applied Sciences equipment.

The number of droplets and particles per latex liter (N_d and N_p) and their ratio (N_p/N_d) were obtained from the x data and the DLS measurements of $\bar{d}_d$ and d_p. They were calculated by considering the volume of droplets and particles as the addition of the volumes of their components: unreacted monomer and PS (preformed PS and polymerized St). It is noteworthy that both N_d and N_p have some uncertainty because i) droplets and particles were considered to be monodisperse in size; and ii) the third powers of the intensity averages $\bar{d}_d$ and d_p were used in their calculation.

Particle were also observed by transmission electron microscopy (TEM), using a Philips EM 300 (100kV) equipment, and micrographs were taken at different magnifications, depending on the particle size. To avoid destabilization and monomer loss in droplets and particles, the samples were diluted prior to the DLS measurements with a water solution saturated with SLS and St.

RESULTS AND DISCUSSION

Table 2 summarizes the experiments carried out with different type of initiators, and different amounts of preformed PS exhibiting varied molecular weight. In all the experiments, the measured γ values for the formulated miniemulsions were greater than 41 mN/m, indicating the absence of micelles (γ for the SLS solution at the CMC = 32 mN/m). Figure 2a shows the backscattering profiles along 4 h of a ME (that was not polymerized) containing only 4% wbm of HD, as costabilizer, and without incorporating preformed PS. The backscattering flux of this ME along the sample tube showed changes during the assay because the disperse phase was concentrating at the top of the sample, thus producing creaming. Note that the incorporation of 1% wbop of PS_L (ME1) was not enough to avoid creaming (Figure 2b). However, when increasing either the molecular weight of the preformed PS (ME2) or its content (ME8), the stability of the ME was significantly improved (Figure 2c,d). This behavior is in agreement with that observed by Reimers and Schork (1996) for the ME of MMA/PMMA, where creaming became faster when the viscosity-average molecular weight of the incorporated PMMA was reduced. Creaming depends on

Table 2: Summary of ME polymerizations. Conditions and results.

Exp.	Preformed PS	Initiator	$\bar{d}_d$	γ	x [a]	$\bar{d}_p$ [b]	N_p / N_d [c]
	(% wbop)	(% wbm)	[nm]	[mN/m]	[%]	[nm]	
ME1	PS_L (1)	KPS (0.75)	87	50.9	93	106	0.8
ME2	PS_I (1)	KPS (0.75)	124	49.4	94	97	1.8
ME3	PS_H (1)	KPS (0.75)	137	49.3	92	100	2.2
ME4	PS_L (5)	KPS (0.75)	92	52.2	92	85	1.1
ME5	PS_H (5)	KPS (0.75)	223	41.4	88	104	8.6
ME6	PS_L (10)	KPS (0.75)	95	52.7	94	87	1.1
ME7	PS_L (10)	KPS (1.5)	101	54.0	93	95	1.0
ME8	PS_L (20)	KPS (0.75)	141	51.2	94	114	1.6
ME9	PS_H (5)	TBHP/AsAc (1.5)	228	42.5	90	107	8.4
ME10	PS_L (10)	TBHP/AsAc (1.5)	105	53.2	95	101	1.0
ME11	PS_L (20)	TBHP/AsAc (1.5)	131	51.6	96	121	1.1
ME12[d]	PS_H (5)	TBEC (2.1)	209	44.2	46 (73)	136	3.2
ME13[d]	PS_L (20)	TBEC (2.1)	117	53.8	88 (93)	110	1.1
ME14[d]	PS_H (5)	BPO (2.1)	244	41.0	75 (92)	212	1.3
ME15[d]	PS_L (20)	BPO(2.1)	117	53.8	87 (91)	120	0.8

[a] Conversion at 2 h of polymerization (with BPO and TBEC x at 3h are also reported between parentheses). [b] Final particle diameter. [c] Ratio between final particles number and initial droplets number. [d] Polymerization temperature: 80 ºC
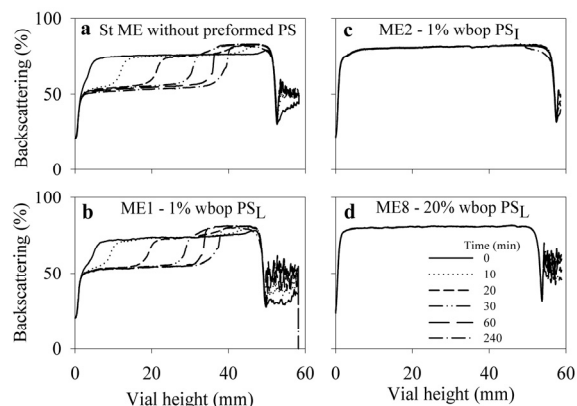

Figure 2: Backscattering data obtained at different times (between 0 and 240 min) and at room temperature, to provide information on the colloidal stability of the miniemulsions.

the droplet size and its distribution, where big droplets tend to concentrate in the upper part of miniemulsions as a consequence of the density difference. But the intensity-based droplet size distribution of ME1 was as broad as that obtained from the stable miniemulsions.

Furthermore, in parallel to backscattering measurements of ME1 (Figure 2b) $\bar{d}_d$ was also monitored, observing an increment of 8 nm after 240 min. and a broadening of the intensity-based droplet size distribution. This could be attributed to droplet coalescence and/or to monomer diffusion. While droplet coalescence depends strongly on surfactant, monomer diffusion is retarded by the costabilizer (Asua 2002). In order to get more insight, an additional

amount of SLS was added to a fresh prepared ME1 to achieve the same fraction of droplet area covered by the emulsifier of ME2, which did not present creaming. However, the incorporation of SLS did not avoid creaming. This could indicate that coalescence was not the main mechanism responsible of creaming and that 1% of PS_L is not enough to retard monomer diffusion.

As expected, $\bar{d}_d$ was increased when the preformed PS content and/or its molecular weight were incremented. With KPS, differences in both polymerization rates (R_p) and droplet nucleation efficiencies were observed, depending on $\bar{d}_d$ and on the concentration and molecular weight of the preformed PS (Table 2 and Figure 3).

With preformed PS_L and with amounts of it ≤ 10% wbop, the viscosity of the organic phase was low enough to obtain a low $\bar{d}_d$ (around 100 nm), which increased the droplet area and allowed a high droplet nucleation when employing a water-soluble initiator ($N_p/N_d \approx 1$, Table 2). Due to the fact that N_p was practically the same, no appreciable differences were found in the resulting R_p. Although the final $N_p/N_d \approx 1$ in ME1, ME4, and ME6; the presence of secondary nucleation was also observed by the evolution of $\bar{d}_p$, with a descendent initial slope, and of N_p (Figure 3). Note that N_p increased at the beginning of the polymerization due to the early formation of new polymer particles by secondary nucleation, while it then decreased as a consequence of the later disappearance of non-nucleated droplets. Secondary nucleation is more probable to occur when water-

soluble initiators (e.g., KPS) are used, yielding hydrophilic radicals that promote the formation of new particles by homogeneous or micelar nucleation [Lopez *et al*., 2011; Goikoetxea *et al*., 2009].

On the other hand, high organic phase viscosities limited the droplet diameter reduction and hence the number of droplets able to be nucleated with radicals coming from the aqueous phase. Note that $\bar{d}_p$ decreased during the polymerization with respect to $\bar{d}_d$ when employing PS_I, PS_H (Figure 3b) or PS_L at 20% wbop (Figure 3e), thus showing the formation of new polymer particles through a secondary nucleation mechanism (Figure 3c,f). It is worth remarking that, in these cases, N_p was always lower than that obtained in the ME polymerization with $\bar{d}_d \approx 100$ nm (ME1, ME4 and ME6), and therefore R_p was a bit reduced (Figure 3a,d). These results are in agreement with those of Costa *et al*. (2013), where ME polymerization became slower when the particle diameter was increased, due to the reduction in the compartmentalization effect.
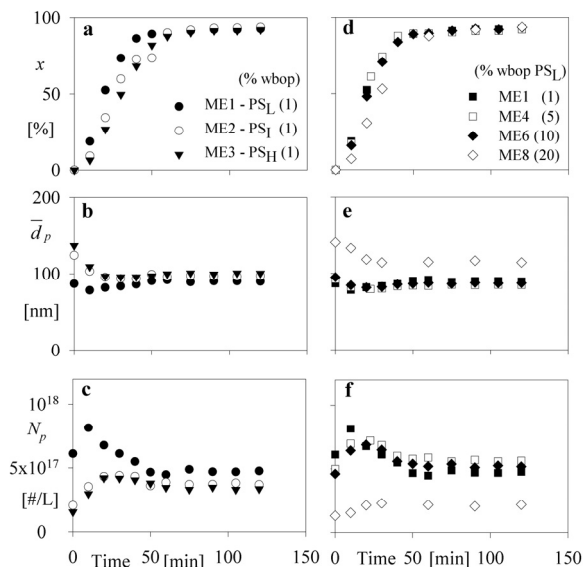

Figure 3: Comparison of St ME polymerizations with KPS and preformed PS of different molecular weights (a-c) and with different PS_L contents (d-f).

Experiments with TBEC and BPO involved higher initiator concentrations, higher temperatures (80 ºC), and extended polymerization times (3 h), because the decomposition rate constants (k_d) at 70 ºC for TBEC ($k_{d(TBPEC)} = 3.27 \times 10^{-7}$ s^{-1} [Brandrup *et al*., 1999]) and BPO ($k_{d(BPO)} = 1.46 \times 10^{-5}$ s^{-1} [González *et al*., 1996]) are lower than for KPS ($k_{d(KPS)} = 2.17 \times 10^{-5}$ s^{-1} [Salazar *et al*., 1998]), and a large fraction of the radicals produced inside the droplets and particles are restricted

to a very small volume, thus promoting bimolecular termination [Autran *et al*., 2007]) Figure 4 compares the evolution of x and $\bar{d}_p$ for the polymerizations that employed KPS, TBHP/AsAc, TBEC and BPO as initiators, for an organic phase containing the same St/PS_L ratio, i.e., similar $\bar{d}_d$.

In experiments with PS_L at 20% wbop (ME8, ME11, ME13 and ME15), and $\bar{d}_d$ a bit higher than 100 nm (117 nm < $\bar{d}_d$ < 145 nm), droplet nucleation was improved by the hydrophobic tert-butoxyl radicals formed by the TBHP/AsAc system, with respect to the water-soluble SO_4^- radicals produced by KPS decomposition, achieving N_p/N_d close to the ideal value of 1 ($N_p/N_d = 1.1$, Table 2). The redox initiator system (TBHP/AsAc) produced an augment of the radical availability, thus increasing the rate of droplet nucleation and therefore R_p. On the other hand, the employment of TBEC and BPO at 80 ºC and 2.1% wbm (ME12 and ME14), produced lower R_p than those obtained with KPS and TBHP/AsAc (ME5, ME8, ME9 and ME11, Figure 4a,c) for similar ME formulations. Also, no significant secondary nucleation was observed when using these oil-soluble initiators, giving place to N_p/N_d of 1.1 and 0.8, respectively.
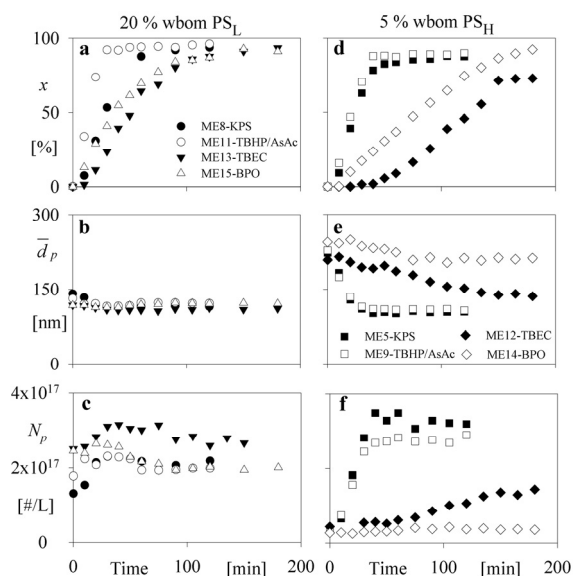

Figure 4: Comparison of ME polymerizations of St with different initiators. Polymerization temperature: 70 ºC with KPS and TBHP/AsAc, 80 ºC with TBEC and BPO.

With 5% wbop of PS_H, the initial $\bar{d}_d$ was higher than 200 nm, similar kinetic behaviour was observed with either TBHP/AsAc or KPS (ME5 and ME9). In this case, $N_p/N_d > 8$ (Table 2) and the evolution of

$\overline{d}_p$ and N_p during the polymerization (Figure 4e,f) gave evidence that most of polymer particles were nucleated by secondary mechanims. In this case, the polymerization proceeded with the monomer diffusion from the non-nucleated droplets through the aqueous phase to the particles formed by secondary nucleation. The similar R_p obtained with KPS and TBHP/AsAc could indicate that, with high secondary nucleation, monomer diffusion controlled R_p instead of the radical generation.

Secondary nucleation was clearly reduced when employing oil-soluble initiators such as TBEC or BPO (ME12 and ME14), since radicals are formed inside the droplets and their water solubilities are limited (water solubility of TBEC = $2.6x10^{-4}$ g/ 100 g, estimated at 25 ºC with Wskowwin v1.42, and of BPO = $3x10^{-4}$ g/ 100 g [Yalkowsky and Banerjee 1992]). With TBEC (ME12), droplet nucleation was increased with respect to KPS (ME5) and TBHP/ AsAc (ME9), but a large number of particles were still formed by secondary nucleation (N_p increased up to N_p/N_d = 3.2). This is probably due to the desorption of tert-butoxyl radicals (formed by TBEC descomposition inside the droplets) to the aqueous phase, which may nucleate new particles by secondary mechanims. The radical desorption from the oil phase was previously reported by Alduncin *et al.* (1991) in the ME polymerization of St using the oil-soluble initiator AIBN. However, when employing BPO as initiator (ME14), the N_p is practically constant, achieving a better N_p/N_d ratio (N_p/N_d = 1.3). Benzoyloxyl radicals are more hydrophobic than tert-butoxyl radicals and, for this reason, their desorption is less probable.

Figure 5 shows the distributions of the droplets and the final latexes for the experiments ME5, ME9, ME12 and ME14. Note that in all cases the intensity-based droplet-size distributions were broad. In ME5 and ME9 (Figure 5a,b) the big droplets disappeared as the polymerization proceeded, thus producing narrow size distributions for the final latexes, containing a high fraction of small particles formed by secondary nucleation. Clearly, big droplets were not nucleated by radicals produced in the aqueous phase. Also, the presence of secondary nucleation, probably by desorption of tert-butoxyl radical formed during the TBEC decomposition inside the droplets, generates narrow size distributions compared to the ME droplet size distribution (Figure 5c). Finally, when BPO was used, the intensity-based size distributions of droplets and particles were similar and the volume PSD measured by CHDF clearly showed the presence of big particles (Figure 5d), thus indicating that

droplet nucleation was the predominant site of particle formation. TEM image for the final latex of ME14 (Figure 6) shows a broad particle size distribution with the presence of big particles, that can be only formed by droplet nucleation.
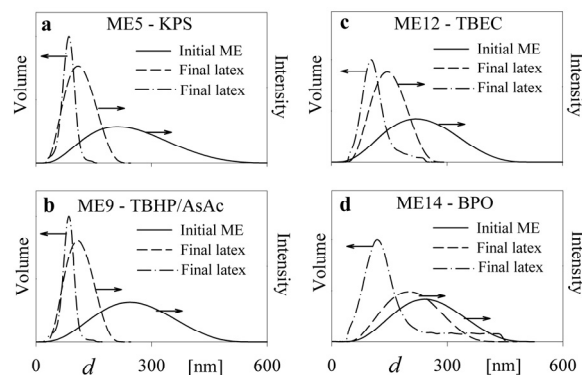

Figure 5: Volume PSD (measured by CHDF) and intensity-based size distributions (measured by DLS) for the experiments with 5% wbop of PS_H and different initiator systems.
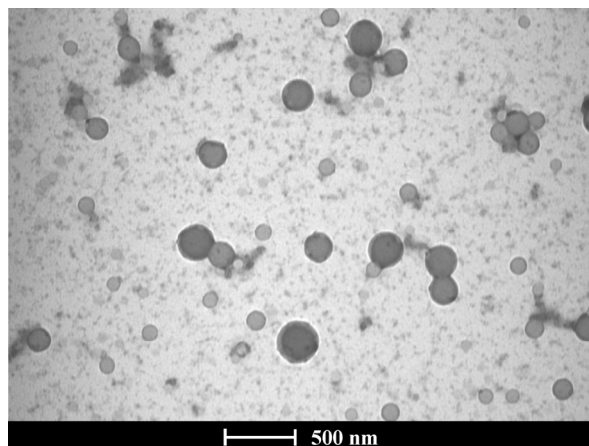

Figure 6: TEM micrography of the final latex particles obtained in ME14 with 5% wbop of PS_H and BPO as initiator.

CONCLUSIONS

Droplet nucleation depends strongly on the combination between the initiator type employed and the ME droplet size. When droplet sizes were between 100–140 nm, significant droplet nucleation was achieved with either water-soluble or oil-soluble initiators, independent of the phase affinity of the radicals produced. With droplet sizes bigger than 200 nm and water-soluble initiators (e.g., KPS or TBHP/ AsAc), high secondary nucleation was produced. In this case, the droplet size was not small enough to

favor their nucleation when the radicals are formed in the aqueous phase. However, the use of the oil-soluble initiators TBEC or BPO improved droplet nucleation. But with TBEC even significant secondary nucleation was still observed, promoted by desorption from the polymer particles of the tert-butoxyl radical, which is less hydrophobic than the other radical, 2-ethylhexyl carbonate. Finally, droplet nucleation could be strongly favoured with the oil-soluble initiator BPO that produces highly hydrophobic radicals.

The results presented in this work could be used as a guide for choosing the phase affinity of the initiator and the radicals produced to achieve the required contribution of droplet nucleation, which in turn depends on the droplet size of the ME. Finally, it should be remarked that the results may differ if the organic phase (monomers and preformed materials) and/or solids content are varied.

ACKNOWLEDGEMENTS

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