(Cryo)-TEM assessment of droplet nucleation efficiency in hybrid acrylic/CeO_2 semibatch miniemulsion polymerization

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Abstract

Monomer droplet nucleation has been successfully tracked in a seeded semibatch miniemulsion polymerization with miniemulsion feeding. Taking advantage of the marker capacity of CeO_2 nanoparticles two polymerizations were designed. In the first one the seed contained nanoceria while a blank monomer miniemulsion was fed to the reactor and in the second reaction the opposite was done; namely, the seed did not contain any CeO_2 and the miniemulsion fed did. In this way, the presence of the CeO_2 in either seed or nucleated particles allowed tracking the fraction of droplets that efficiently nucleated during miniemulsion feeding. Conventional TEM and cryo-TEM were used to monitor the nucleation efficiency by analyzing separately the particle that did or did not contain CeO_2 nanoparticles.

Introduction

Miniemulsion polymerization has become a very powerful technique to synthesize hybrid inorganic/polymeric nanocomposites. The versatility of the technique together with the synergetic effects that can be achieved combining inorganic materials with organic polymers, contributes to obtain materials with different properties and morphologies[1–5]. One of the challenges of the industrialization of the miniemulsion polymerization technology is the requirement of running the polymerizations under semibatch conditions to control the reaction temperature[6]. In order to run semibatch polymerizations with hybrid systems, it is necessary to feed a hybrid miniemulsion to the reactor. The goal under this procedure is to nucleate the highest number of droplets to avoid monomer diffusion to the seed particles (that might lead to segregation of the organic or inorganic material, as it has been described in previous works[7]) and to obtain polymer particles with similar hybrid morphologies.

In spite of the importance of this technology, little attention has been devoted in the open literature to the understanding of the droplet nucleation under semibatch miniemulsion feeding conditions. One of the reasons for this lack of attention can be likely found on the difficulties of tracking the new polymer particles formed from the entering nanodroplets. Thus, the analysis of the particle size distributions (PSDs) measured by means of Capillary Hydrodynamic Fractionation (CHDF)[8,9] along the feeding period and the use of blue dyes as markers of the nanodroplets[10–12] and therefore, of the nucleated polymer particles have been the most interesting attempts to analyze the efficiency of the droplet nucleation. Rodriguez et al.[8] shed light on the nucleation efficiency of the entering nanodroplets, based on the PSDs measured along the reaction. They concluded that the nucleation of the fed miniemulsion droplets was substantial at the beginning of the feeding period and decreased as the feeding time increased, leading to a large fraction of monomer droplets non-nucleated or if they nucleated, to smaller particles because an important fraction of the monomer diffused out of the droplets to the existing particles. The explanation for this behavior was the competition for the capturing of the radicals by the seed particles and the entering monomer nanodroplets. However, they could not discriminate by CHDF in the low particle size region whether these particles were synthesized by homogeneous nucleation or by late nucleation of the nanodroplets that were depleted of monomer.

Chern et al.[13] used an hydrophobic blue dye to determine the loci of particle nucleation during a batch miniemulsion polymerization. The particles formed in the aqueous phase did not contain any dye since the transport of these dye molecules from the monomer droplets through the aqueous phase was unlikely, due to their extremely low water solubility. In that way they were able to detect homogeneous nucleation taking place during the polymerization process. However, the separation between the particles containing dye was done by precipitation and this introduces important uncertainties in the computation of the efficiency of the nucleation. Furthermore, the implementation of this method in a semibatch process is rather difficult because particles without dye will form in the batch and semibatch processes.

We have recently shown the synthesis of hybrid acrylic/CeO_2 latexes with encapsulated morphology by a two step seeded semibatch miniemulsion polymerization process[14–16]. One of the main features observed was that the amount of particles without nanoceria was almost negligible, nanoceria did not migrate to the aqueous phase, and they could be tracked easily in TEM micrographs. Furthermore, it was observed that the size of the CeO_2 aggregates did not change from the seed to the final polymer particles, indicating that there was not exchange of the CeO_2 nanoparticles neither through the aqueous phase nor by collision of the droplets/particles. In other words, it was possible to track the fate of the nanodroplets that contained CeO_2 nanoparticles along a reaction. The experiments carried out in our previous work[7] were not designed to analyze the efficiency of the droplet nucleation and hence were not conclusive. Nonetheless, they guide us to design seeded semibatch miniemulsion polymerization experiments to shed light on the efficiency and droplet nucleation mechanism in a substantially less unambiguous way than it has been done in previous literature works[8,10–12].

Therefore, in this work, two seeded semibatch miniemulsion polymerizations were designed to track droplet nucleation by monitoring the particles that contained CeO_2 nanoparticles by means of TEM analysis. The two experiments are schematically described in Figure 1.

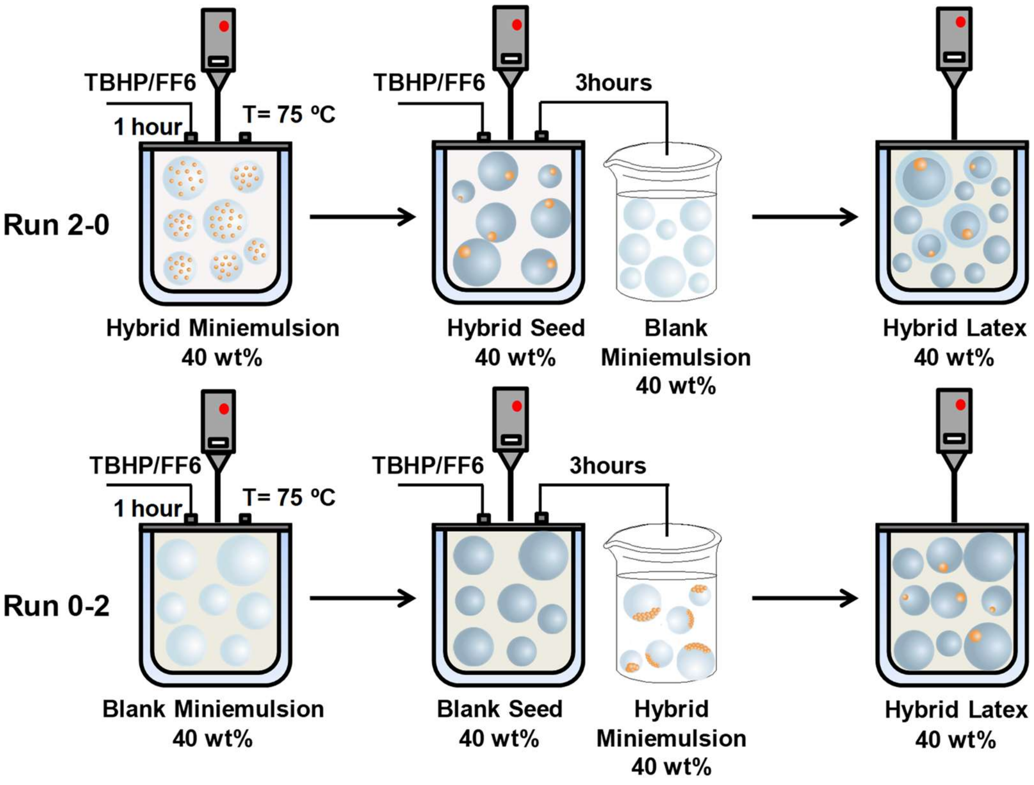


Figure 1. Scheme of the polymerization process for runs Run 2-0 and Run 0-2.

In the first experiment the seed was prepared by using a hybrid miniemulsion that contained 2 wbm% of CeO_2 and a neat monomer miniemulsion was fed to the reactor for 3 hours (Run 2-0). In the second experiment the reverse was done; namely, the seed was prepared without CeO_2 by miniemulsion polymerization and the miniemulsion fed contained CeO_2 (Run 0-2) in a 2 wbm%. This work analyzes in an unambiguous way the evolution of the droplets (polymer particles) that do and do not contain CeO_2 by means of (cryo)-TEM along the reaction to understand the fate of the nanodroplets during the semibatch addition of a miniemulsion.

Experimental section

Materials

The CeO_2 nanoparticle dispersion (49 wt% in mineral spirit, Altana), was dried (at 60 °C for two days) and grinded before using. The average size of the CeO_2 nanoparticles dispersed in the monomer mixture was of 12 nm measured by DLS (see Supporting Information). Methyl methacrylate, MMA (Quimidroga), n-Butyl acrylate, BA (Quimidroga) and Acrylic acid, AA (Aldrich) were used as received. tert-Butyl hydroperoxide (TBHP, Aldrich) and FF6 (Brüggemann Chemical, Heilbronn) initiators were used as supplied. Dodecyl diphenyloxide disulfonate (Dowfax 2A1, 45%, Dow Chemicals) and n-Octadecyl acrylate (97%, Aldrich) were used as an anionic emulsifier and as a co-stabilizer, respectively. Deionized water was used in the miniemulsions and hydroquinone (Aldrich) was used for stopping the reaction in the samples withdrawn from the reactor.

A copolymer, poly (MMA-*co*-BA-*co*-AA), synthesized by solution polymerization was used to enhance the stability of the miniemulsions. The composition was 49.5 wt% MMA, 49.5 wt% BA, 1 wt% AA with a final molecular weight of 62000 g/mol and 2.3 of dispersity. It was dried before using in a vacuum oven at 50 °C for 24 h.

Miniemulsion preparation

Hybrid miniemulsions with 40% solids content and with (2 wbm%) or without CeO_2 were prepared. The formulations used to prepare the miniemulsions are presented in Table 1. The oil phase was prepared by mixing the monomer mixture MMA (49.5wt %) / BA (49.5wt %) / AA (1wt %), the costabilizer (Octadecyl acrylate), the nanoceria (if present) and the copolymer (poly(MMA-*co*-BA-*co*-AA)). This mixture was stirred under magnetic agitation for 15 min at 800 rpm. The aqueous phase was obtained by dissolving the emulsifier (Dowfax) in water. Both, organic and aqueous phases were brought together and mixed magnetically for 15 min. The resulting dispersions were then sonified using a Branson 450 equipment (operating at 8-output control and 80 % duty cycle for 5 min in an ice bath and under magnetic stirring). After that, a high shear homogenizer (Niro Soavi Panda 2K) was used in order to obtain a narrower droplet distribution (see supporting information), using 40.0 MPa in the first valve and 4.0 MPa in the second stage valve.

Table 1. Formulation used to prepare hybrid miniemulsions containing 40 wt% SC and 2 wbm% CeO_2.

	Component	Wt (%)
Oil Phase	MMA	19.8
	BA	19.8
	AA	1
	CeO_2*	2
	Octadecyl Acrylate*	4
	Poly(MMA-co-BA-co-AA)*	0-10
Water Phase	Dowfax*	2
	Deionized water	60

*With respect to the monomer

Miniemulsion polymerization

As depicted in Figure 1 two seeded semibatch miniemulsion polymerizations were carried out. The seed was produced by loading the miniemulsion, 35 wt% of the final latex content (in Run 2-0 the miniemulsion contained CeO_2 and in Run 0-2 it did not) in the reactor and polymerizing it at 75 °C for 60 minutes, while the initiators (0.5 wbm% with respect to the initial amount of monomer in the miniemulsion) were fed to the reactor. Then, the remaining initiator (0.5 wbm% with respect to the monomer fed) was added and other miniemulsion (in Run 2-0 it did not contain CeO_2 and in Run 0-2 it did) was fed into the reactor for 3h. The initiator (the redox pair TBHP/FF6) was fed to the reactor during the whole polymerization period. Temperature was increased up to 90 °C and the cooking was done for 1 hour in all the cases after the 3h of feeding.

Characterization methods

Polymer particle and monomer droplet sizes distributions were measured by Dynamic Light Scattering (DLS) using a Zetasizer Nano Series (Malvern Instrument). For this analysis, a fraction of latex (or miniemulsion) was diluted with deionized water. The reported average particle size (droplet size) values represent an average of two repeated measurements. Conversion was measured gravimetrically. The stability of the miniemulsions was studied by measuring the backscattered light at 60 °C in the Turbiscan Lab expert equipment.

The morphology and PSD of the polymer particles were analyzed by Transmission Electron Microscopy (TEM), in a TECNAI G2 20 TWIN (FEI), operating at an accelerating voltage of 200 KeV in a bright-field image mode. The samples were diluted and then, they were dried using a UV lamp. On the other hand, the preparation of the cryo-TEM samples first involved a vitrification procedure on a FEI Vitrobot Mark IV (Eindhoven, The Netherlands). One drop of the sample solution (~3 μL) was deposited in a copper grid (300 mesh Quantifolis, hydrophilized by glow-discharged treatment just prior to use) within the environmental chamber of the Vitrobot and the excess liquid was blotted away. The sample was shot into melting (liquid) ethane and transferred through 655 Turbo Pumping Station (Gatan, France) to a 626 DH Single Tilt Cryo-Holder (Gatan, France), where it was maintained bellow - 170 ºC (liquid nitrogen temperature). The sample was examined in the TECNAI G2 20 TWIN (FEI) mentioned above, operating at an accelerating voltage of 200 keV in a bright-field and low-dose image mode.

PSD of the polymer particles with and without CeO_2 nanoparticles was analyzed by the software Image Pro Plus 7.0.

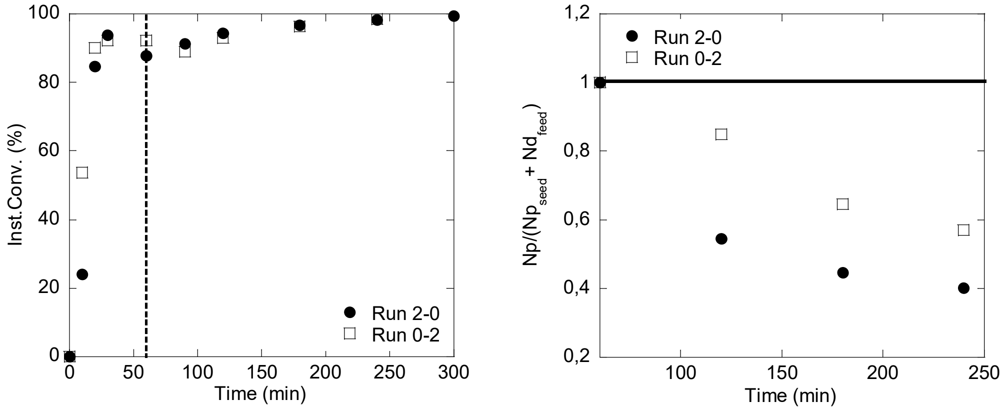
Results and discussion

Table 2 presents the final conversions, the average droplet and particle sizes measured for both runs by DLS. In both polymerizations total conversion was achieved and the feeding was done under starved conditions as it is presented in Figure 2a.

Table 2. Summary of Run 2-0 and Run 0-2 polymerizations: the final conversion (%), initial droplet size ($Dd_{initial}$,nm), seed particle diameter (Dp_{seed},nm), feeding droplet size ($Dd_{feeding}$,nm) and final particle diameter (Dp_{final},nm) are presented.

	Conv. (%)	$Dd_{initial}$ (nm)	Dp_{seed} (nm)	$Dd_{feeding}$ (nm)	Dp_{final} (nm)
Run 2-0	99	142	129	138	174
Run 0-2	100	120	112	145	156

The initial droplet sizes were clearly affected by the presence of CeO_2 nanoparticles in the formulation (see Table 2). Thus, the miniemulsion used to prepare the seed of Run 2-0 and the miniemulsion fed in Run 0-2 contained CeO_2 nanoparticles and yielded similar sizes of 142 nm and 145 nm, respectively. On the other hand, the miniemulsions that did not contain CeO_2 yielded smaller droplet sizes (120 and 138 nm). In both cases, the particle diameter obtained in the seed (after the batch process) slightly decreased from the initial droplet size.



a) **b)**

Figure 2. a) Instantaneous conversion and b) $Np/(Np_{seed}+Np_{feed})$ evolution during the polymerization for Run 2-0 and Run 0-2. The horizontal line represent the theoretical evolution of $Np/(Np_{seed}+Np_{feed})$ if all entering droplets do nucleate.

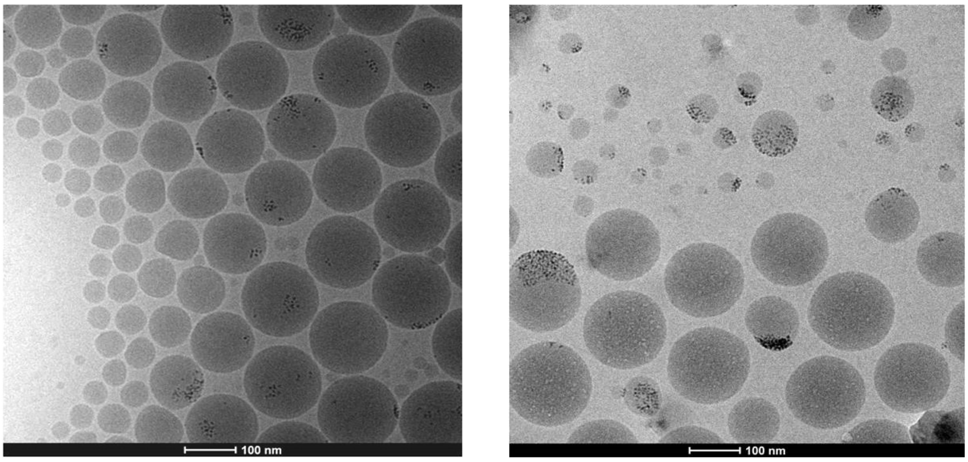
The Z-average particle diameter (measured by DLS) increased during the feeding period in both polymerizations (see supporting information). Figure 2b presents the evolution of the ratio of the number of particles vs the number of seed particles plus the fed monomer droplets $Np/(Np_{seed}+Nd_{feed})$; Np_{seed} and Nd_{seed} calculated from the intensity average particle and droplet sizes measured by DLS. N_p was determined following Equation 1,

$$N_p = \frac{6 \cdot (M_0 X/\rho_{pol})}{\pi \cdot {d_p}^3} \tag{1}$$

where M_0 is the amount of monomer fed up to the sampling time (g), X is the overall monomer conversion, ρ_{pol} is the polymer density (1.135 g/cm^3) and d_p is the intensity average particle size (cm) calculated from the DLS, that accounts for the polymer particles and the small fraction of non-nucleated nanodroplets present in the reactor at the sampling time.

The horizontal line represents the value of $Np/(Np_{seed}+Nd_{feed})$ when all the entering droplets nucleate; namely, 100% efficiency of droplet nucleation. Figure 2b shows a fraction of the entering nanodroplets nucleated because $Np/(Np_{seed}+Nd_{feed})$ values corresponding to complete absence of droplet nucleation are smaller than the values achieved at the end of the polymerization (for Run 2-0 0.33 and for Run 0-2 0.45).

A more detail information about the fate of the entering droplets can be obtained by tracking during the feeding time the particles that do contain or not CeO_2. Figure 3 presents the cryo-TEM micrographs of the hybrid latexes Run 2-0 and Run 0-2 obtained after polymerization (in the supporting information the TEM images taken at 60, 120, 180 and 300 min of reaction for each case are shown). Thanks to the easy tracking of CeO_2, the particles coming from the seed can be clearly identified all along the reaction in Run 2-0 (the ones containing nanoceria particles). The images show that the particles containing CeO_2 were larger in size, while the blank particles were smaller. However, for Run 0-2 the difference in size between the particles containing CeO_2 or the blank ones was not so pronounced (Figure 3), but notably the small particles contained ceria. Thus, in order to confirm this qualitative observation, the PSD of both populations (particles with and without CeO_2) during the polymerization process were determined from the TEM micrographs.

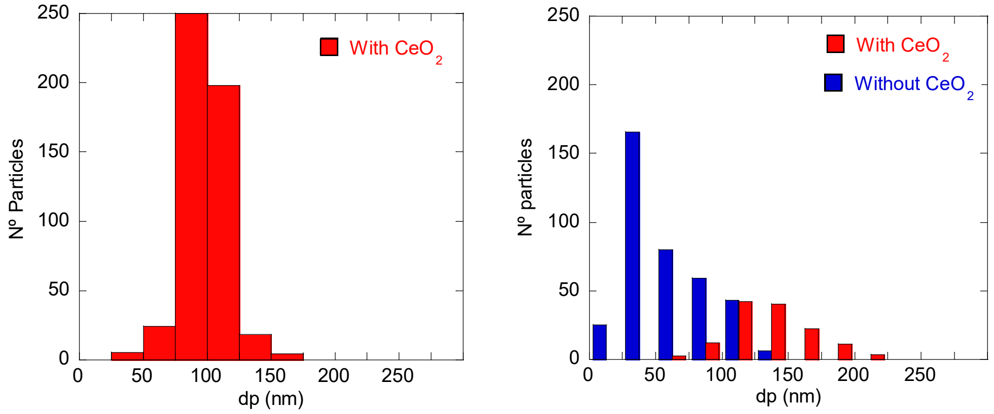


Run 2-0 **Run 0-2**

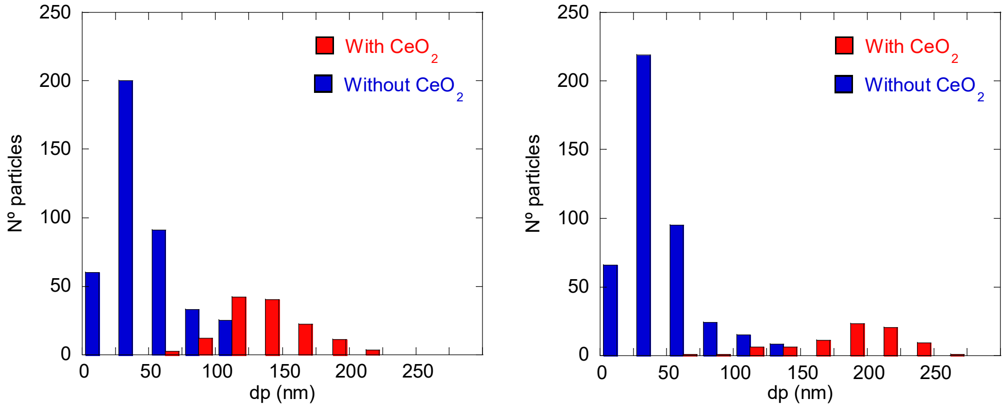
Figure 3. cryo-TEM micrographs of the hybrid latexes for Run 2-0 and Run0-2, at the end of the polymerization process.

Figure 4 and 5 present the evolution of the particle size distributions obtained upon analyzing 500 hybrid (in red) and neat particles (in blue) from TEM images, for Runs 2-0 and 0-2, respectively.

For Run 2-0 after the seed polymerization (60 min) the size of the particles containing nanoceria was in the range 50-175 nm, and it can be observed that this population (in red on the PSDs) grew in size during the feeding process likely due to monomer diffusion from the entering nanodroplets (Ostwald ripening); the larger particle of the distribution moved from 175 to 275 nm and besides the fraction of large particles increased too. At the end of the polymerization, the particles containing nanoceria were between 50-275 nm whereas sizes not larger than 125 nm were measured for the neat particles. Note, that the average droplet size of the miniemulsion fed was 138 nm (see Table 2). It can be concluded that a bimodal distribution was formed during the polymerization process, with the larger particles corresponding to the ones coming from the seed and the smaller ones to the fed nanodroplets.



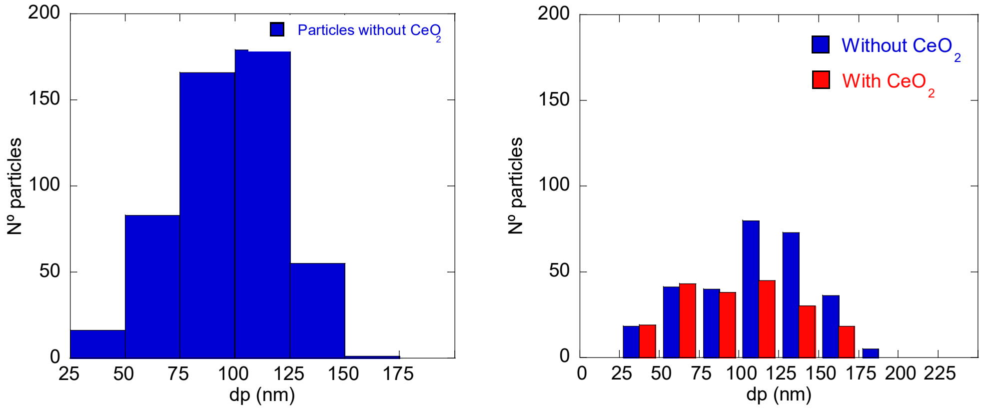
60 min **120 min**



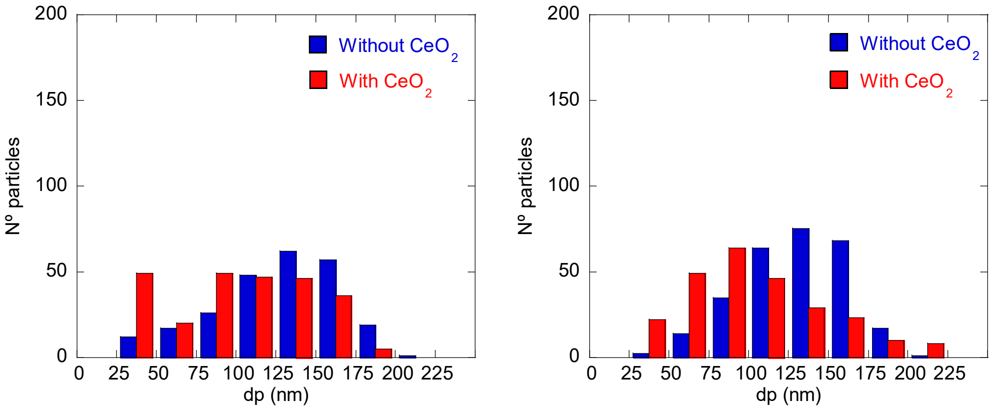
180 min **300 min**

Figure 4. Particle size distributions of polymer particles with and without CeO_2 nanoparticles at different reaction times for Run 2-0.

In Run 0-2, the seed was made of neat polymer particles and the fed nanodroplets contained nanoceria. This time, at 60 min the seed particles sizes (neat ones) were between 25-175 nm. Along the reaction this population grew in size reaching values in the range of 50-225 nm due to transport of monomer from the fed miniemulsion.



60 min **120 min**

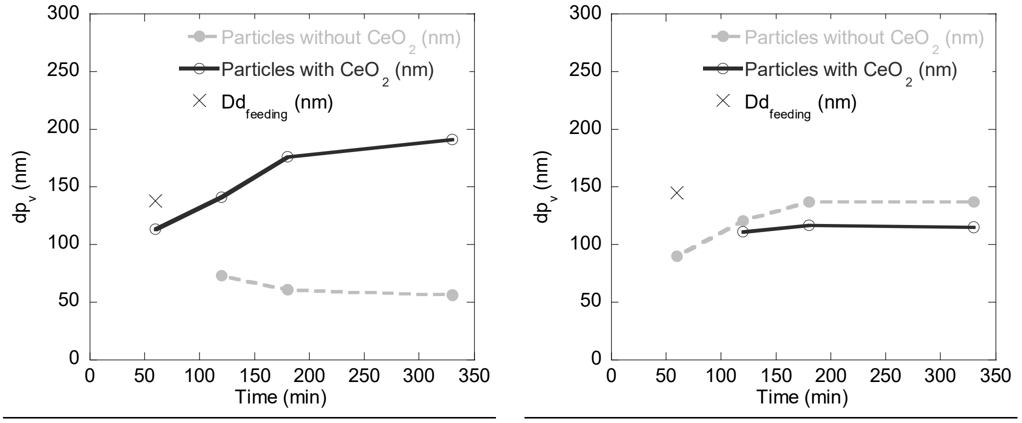


180 min **300 min**

Figure 5. Particle size distributions of polymer particles with and without CeO_2 nanoparticles at different reaction times for Run 0-2.

However, the PSDs show that the entering hybrid nanodroplets nucleated more efficiently than the neat nanodroplets fed in Run 2-0. This can be attributed to the enhanced stability of the miniemulsions that contain CeO_2 nanoparticles[14](see also supporting information). The final PSD of the latex was broad but not bimodal as that of Run 2-0.

The time evolution of the volume average particle sizes of particles with and without nanoceria, calculated from the TEM PSDs, are presented in Figure 6. It can be clearly seen that in Run 2-0, the size of the particles of the seed (with CeO_2) increased in size in a larger extent than the seed particles (without CeO_2) of Run 0-2. Moreover, it can be seen that the nucleation efficiency of the nanodroplets fed during 3 hours was different in both runs. Whereas in Run 2-0 the size of the particles nucleated from the fed nanodroplets continuously decreased during the feeding time, in Run 0-2 it was rather constant indicating that a high number of droplets nucleated and less monomer was transferred from the entering droplets to the polymer particles in the reactor (note that the size of the particles was around 100 nm and the average size of the entering nanodroplets was 145 nm). Altogether, these figures indicate that droplet nucleation efficiency of the miniemulsions fed was substantially higher for Run 0-2 where the miniemulsion fed contained CeO_2. According to Rodriguez et al. the nucleation efficiency is related to the stability of the minemulsion fed (the higher the stability the higher the nucleation of the entering droplets) and also to the ratio of the number of entering droplets with respect to the number of particles in the seed (the higher this ratio, the higher the number of fed droplets that nucleate because their efficiency for capturing radical is higher). For the two experiments of this work this ratio ($N_{droplets\_fed}/N_{seed}$) was larger for Run 2-0 (Table 2); therefore this cannot be the reason for the enhanced droplet nucleation found for Run 0-2, but the enhanced stability of the miniemulsion fed (whose only difference was that the one for Run 0-2 contained CeO_2 nanoparticles). As shown in the supporting information the stability measured to both miniemulsions indicate that the one containing nanoceria (Run 0-2) was more stable than that of the pristine one (Run 2-0).



Run 2-0 **Run 0-2**

Figure 6. Average particle size (in volume) evolution during the reaction for both populations with and without containing CeO_2. The x represents the size of the fed monomer droplet size measured by DLS.

Table 3 presents the ratio Np/Np_{seed} calculated at the end of the polymerization from the cryo-TEM micrographs (as Np_{seed} only the particles that contain CeO_2 are considered in Run 2-0 and the blank ones in Run 0-2; Np accounts for all type of particles) and the theoretical value expected if all the fed nanodroplets would have nucleated. This later value was calculated from the average particle and droplet sizes measured by DLS (see Table 2). Although the fact that only 500 particles were counted for each reaction might introduce some uncertainty in the experimental values, it is interesting that both values are very close in both theoretical and experimental analysis. This close values indicate that most of the entering nanodroplets do nucleate even though an important amount of the monomer diffused out of the droplets; the higher the stability of the miniemulsion the lower the amount of monomer lost by diffusion.

Table 3. Np/Np seed values for Run 2-0 and Run 0-2. The theoretical value is calculated using DLS dp_{seed} and dd_{fed} results whereas the experimental is calculated using cryo-TEM data from the distributions of Figure 4 and 5.

Np/Np_{seed}	Run 2-0	Run 0-2
Theoretical	3.0	2.2
Exp. Cryo-TEM	3.1	2.6

According to these detail analysis droplet nucleation efficiency in miniemulsion feeding is more sensitive to the stability of the entering miniemulsion than to the radical capturing competition between the experiments entering nanodroplets and the already existing polymer particles.

Conclusions

It was demonstrated that the use of CeO_2 nanoparticles as marker, in specifically designed seeded semibatch miniemulsion polymerizations, coupled with TEM analysis is a powerful technique to understand the efficiency of droplets nucleation in semibatch miniemulsion polymerization.

It was found that the nucleation efficiency of the monomer droplets in semicontinuous addition is more sensitive to the stability of the miniemulsion than to the radical capturing efficiency of the entering nanodroplets (ratio $Np_{droplets\ fed}/Np_{seed}$). Furthermore, for the MMA/BA/AA copolymer latexes used as model systems in this work, it was unambiguously found that the bimodal PSD obtained at the end of the semibatch miniemulsion polymerization was not due to secondary nucleations (either micellar or homogeneous nucleation) but to late nucleation of the fed monomer droplets upon depleting most of their monomer by diffusion to the seed particles or to the early nucleated monomer droplets. The presence of the CeO_2 in the small population of particles allows discriminating between the two potential sources of this crowd of particles, which was not possible using only PSD chromatograms.

The approach proposed in this work opens the possibility to understand in great detail the fate of nanodroplets fed during semicontinuous miniemulsion polymerization and also indicates that in order to increase the efficiency of droplet nucleation in the synthesis of hybrid (organic-organic and organic-inorganic) latexes by seeded semibatch miniemulsion polymerization, efforts should be directed to improve the stability of the hybrid miniemulsions.

Acknowledgements

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