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Synthesis of Core-Shell Particles with Low Molecular Weight Alkanes by Miniemulsion Polymerization

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Summary: Miniemulsion polymerization technique was used to obtain core-shell nanoparticles with a core of low molecular weight alkanes and a polystyrene shell. Reactions were performed at 80°C for 5 hours using benzoyl peroxide as oil-soluble initiator. The effect of different alkane types, namely n-hexadecane, n-octane and n-heptane, and initiator concentrations on reaction rates, particle sizes, molecular weights and particles morphology were evaluated. When shorter chain alkanes as n-heptane and n-octane were used it was observed lower reaction rates, higher particle sizes and less sharp particle morphology than in reactions with hexadecane in which well formed core-shell particles were obtained. These results were assigned to the plasticizing effect and higher water-solubility of n-octane and n-heptane, responsible for decreasing the gel effect and favoring the diffusional degradation.

Keywords: alkanes; core-shell polymers; kinetics (polym.); miniemulsion polymerization; nanoparticles

Introduction

Polymeric nanoparticles have been intensely investigated in recent years, especially the structured ones. Structured particles include polymeric particles with core-shell morphology, which consist of a polymeric shell and a core of another polymer or of an encapsulated liquid. Core-shell particles with polymeric core are usually obtained aiming at the improvement of the physical and chemical properties of these materials.[1,2] When the core is liquid, either nanocapsules or hollow particles can be obtained, according to the liquid used and the final product application. In this way, nanocapsules are obtained when a liquid is encapsulated by a polymeric shell and remains into it, such as in drug delivery systems, healing agent carriers for repair methods or thermal storage/control systems with phase-change materials.[3–5] Hollow particles can be obtained by expansion/swelling or encapsulation of volatile liquids and are applied mainly as opacity agent in architectural and paper coatings, partially replacing titanium dioxide and increasing the abrasion and wet scrub resistance of the films.[6]

Several techniques have been reported in order to obtain core-shell nanoparticles, however in the last decade the miniemulsion polymerization technique has been receiving great attention.[7–12] In direct miniemulsion systems the organic phase is dispersed into an aqueous phase by the application of a high shear resulting in droplets with diameter between 50 and 500 nm. These systems are usually composed by monomer, water, surfactant and co-stabilizer. The co-stabilizer, a highly water insoluble compound, suppresses or minimizes the diffusional degradation (also kwon as Ostwald ripening) and the consequent disappearance of the smaller droplets, and the surfactant, mostly adsorbed on the submicrometric droplets surface, prevents the droplets degradation by coalescence. Thus, particle nucleation occurs primarily by the droplet nucleation mechanism, offering advantages for the incorporation of hydrophobic compounds since

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mass transfer between the phases is not required.[13–16]

Usually, the formation of core-shell nanoparticles by direct miniemulsion polymerization takes place due to a phase separation of the hydrophobic liquid from the polymeric phase as long as it is a solvent of the monomer and a non-solvent of the polymer.[17] Thus, organic liquids such as triacylglycerols,[9,10] liquid wax esters,[12] paraffin[8] and hexadecane[12,18,19] are mostly used to obtain core-shell nanoparticles with a liquid core. The encapsulation of short chain alkanes is difficult due to their lower hydrophobicity that leads to a more pronounced diffusional degradation of the miniemulsion and only a reduced number of works reported the synthesis of core-shell nanoparticles with encapsulated iso-octane,[20–22] but none of them involved the encapsulation of other short chain alkanes.

Recently, in a previous work of the group, Capeletto et al.[19] carried out the incorporation of n-octane and n-heptane in polystyrene (PS) nanoparticles by miniemulsion polymerization, though limited to low concentrations of alkanes, namely 4.5, 8.6, 12.4 and 15.9% related to the organic phase.

Higher amounts of short chain alkanes inside polymer nanoparticles could impact positively particle expansion and, thus the formation of submicrometric hollow particles. Therefore, the present study shows the investigation of the encapsulation of short chain alkanes in PS nanoparticles by miniemulsion polymerization. The alkanes evaluated include n-octane and n-heptane (44% on the organic phase) and were compared to n-hexadecane, also used as co-stabilizer in all cases at a concentration of 6.0 wt% on the organic phase. The influence of initiator concentration and alkane type on kinetics, particles size, molecular weight and morphology were evaluated.

Experimental Part

Materials

Polymerization reactions were carried out with styrene (Sty, Innova S.A.) as main monomer, methacrylic acid (MAA, BASF) as hydrophilic co-monomer, n-hexadecane (HD, Vetec Química) as co-stabilizer, sodium lauryl sulfate (SLS, Vetec Química) as surfactant and benzoyl peroxide (BPO, Sigma-Aldrich S.A.) as initiator. N-octane and n-heptane (both Vetec Química) were used as compounds to be encapsulated, in addition to HD. All reagents were used as received and distilled water was used as continuous phase. It was also used hydroquinone (Nuclear) to inhibit the reaction during the gravimetric analysis and tetrahydrofuran (THF, JT Baker) to solubilize the polymer in the gel permeation chromatography analysis.

Miniemulsion Polymerizations

The miniemulsions were prepared with about 20.0 wt% of organic phase of which 50.0 wt% were monomers and 50.0 wt% were alkanes. The monomers include Sty (49.5 wt%) and the hydrophilic co-monomer MAA (0.5 wt%), and the alkanes include HD (50.0 wt% in HD reactions and 6.0 wt% in the remaining), n-octane (44.0 wt% only in OCT reactions) and n-heptane (44.0 wt% only in HEP reaction). The surfactant and initiator amount used were 1.0 wt% on organic phase and 1.0 or 2.0 mol% on monomers, respectively. The formulations details are shown in Table 1.

The organic phase was prepared mixing the monomers, the initiator and the alkanes in a jacketed glass reactor with magnetic stirring at 20°C for 20 min, then this organic phase was added to the aqueous phase (distilled water and surfactant) and stirred for more 10 min. In sequence, the macroemulsion was sonicated with an ultrasonic probe (Sonic Dismembrator 500, Fisher Scientific) at 20°C and 70% amplitude during 1 min. Once prepared, the miniemulsion was transferred to glass vials and inserted into a thermostatic bath at 80°C to react for 5 hours. For each sampling point a vial was removed of the thermostatic bath and its contents used for analyses. No agitation inside the vials was needed during the

Table 1.
Formulations of miniemulsion polymerizations.

Reagents (g)*	Reactions					
	HD1	HD2	OCT1	OCT2	HEP1	HEP2
BPO	0.07	0.14	0.07	0.14	0.07	0.14
HD	3.00	3.00	0.36	0.36	0.36	0.36
N-octane	–	–	2.64	2.64	–	–
N-heptane	–	–	–	–	2.64	2.64

* Monomers (2.97 g of Sty and 0.03 g of MAA) and aqueous phase (24 g of water and 0.06 g of SLS) were kept the same in all reactions.

reactions due to their small diameters and the miniemulsion stability.

Characterization

Monomer conversion during the reaction was determined based on gravimetric analysis.

The polymer particles size distribution (PSD) and z-average diameter (Dp) were determined by Dynamic Light Scattering (DLS – Zetasizer Nano S ZEN1600, Malvern Instruments). For this analysis, samples were diluted in water saturated with monomer in proportion of 1:25 (v/v).

The molecular weight distribution and number- and weight-average molecular weight (Mn and Mw, respectively) were determined by gel permeation chromatography (GPC) in a High Performance Liquid Chromatograph (HPLC LC-20A, Shimadzu) with three columns Shim-Pack GPC-800 Series 300 × 8 mm in series (GPC-801, GPC-804 and GPC-807) and a refractive index detector (RID-10A). The samples were solubilized in THF, filtered through a nylon filter with pore size of 0.45 μm and analyzed at 35°C after automatic injection of 20 μL of the solution. The molecular weight results were determined based on a calibration curve using polystyrene standards with molecular weights ranging between 580 and 3.8×10^6 g/mol.

The morphology of the polymeric nanoparticles was determined by transmission electron microscopy at 80 kV (TEM – JEM-1011, JEOL). For this analysis one drop of the diluted sample (1:1 v/v) was placed on a 300 mesh parlodium coated copper grid. To assure representative images several different regions of the TEM grids were analyzed.

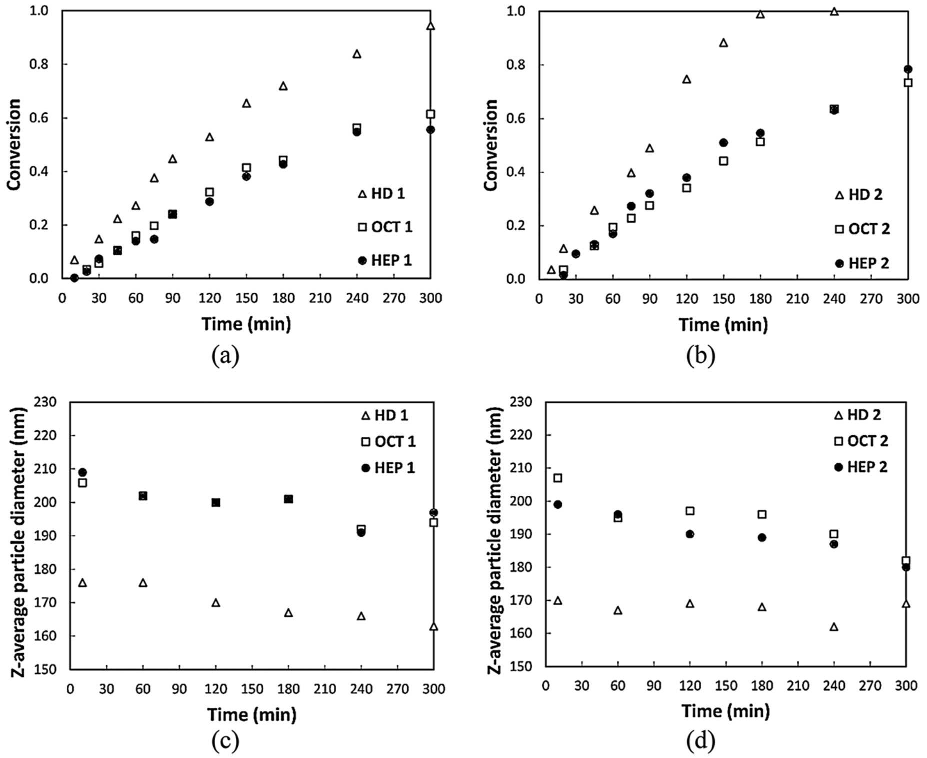
Results and Discussion

Miniemulsion polymerization allows the use of both organo- and water-soluble initiator since the main polymerization *locus* is inside the polymer particles/monomer droplets. Usually water-soluble initiators provide superior reaction rates than organo-soluble ones due to the higher efficiency as a result from their decomposition in the aqueous phase. On the other hand, it was suggested that organo-soluble initiators can reduce the homogeneous particle nucleation.[23] Furthermore, the initiator concentration affects the kinetics and final product properties, as polymer molecular weight and particles morphology since variations in kinetics can lead to a nonequilibrium morphology.[24] Thus, for the alkane types evaluated (HD, n-octane and n-heptane) two different concentrations of the organo-soluble initiator BPO were used, 1 and 2 mol% on the monomer amount. The main results are shown in Table 2 and the evolution of conversion and z-average particle diameter are shown in Figure 1.

At the beginning of the polymerizations, up to around 30% of conversion, the BPO concentration did not significantly affect the reaction rate and reactions conducted with the same alkanes but with different initiator concentrations, as reactions HD 1

Table 2.
Results of styrene miniemulsion polymerizations in the presence of different alkanes.

Properties		HD1	HD2	OCT1	OCT2	HEP1	HEP2
Conversion (%)		94.4	100.0	61.4	73.3	55.6	78.4
Z-Average particle diameter (nm)		163	165	194	182	197	180
Z-Average droplet diameter (nm)		176	174	220	224	212	215
Average molecular weight (g/mol)	Mw × 10^3	85.6	42.6	96.5	52.1	104.3	49.8
	Mn × 10^3	33.8	16.0	33.4	18.5	35.1	17.2
	Mw/Mn	2.5	2.7	2.9	2.8	3.0	2.9



(a) (b)

(c) (d)

Figure 1.
Effect of different alkanes on the evolution of monomer conversion and z-average particle diameter during styrene miniemulsion polymerizations with 1 mol% [(a) and (c)] and 2 mol% [(b) and (d)] of BPO, respectively.

and HD 2, OCT 1 and OCT 2, as well as HEP 1 and HEP 2, presented similar evolution of conversion. These results indicate that under the studied conditions these styrene miniemulsion polymerization using BPO as oil soluble initiator showed a behavior similar to Case II kinetics of the Smith-Ewart theory for emulsion polymerizations.[25] Only after 30% conversion, due to the gel effect (decrease of the frequency of the termination reactions in the polymer particles with a consequent increase in the number of radicals per polymer particle) reactions with higher BPO concentrations presented a higher reaction rate, as observed in Figure 2 with the reaction rate ratios between polymerizations carried out with 2 mol% and with 1 mol% of BPO. Radicals formed by the dissociation of an oil soluble initiator inside the droplets/

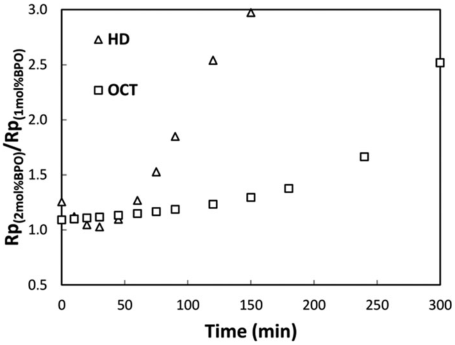


Figure 2.
Comparison between reaction rate ratios of styrene miniemulsion polymerizations with 2 and 1 mol% of BPO in the presence of HD or n-octane.

particles are restricted to a very small volume and, thus, the probability of termination is very high decreasing the efficiency of these radicals to start polymerization.[26] Therefore, miniemulsion polymerizations using oil soluble initiators as BPO may also show a behavior according to Smith-Ewart Cases. Styrene polymerizations, due to the relatively low solubility of styrene in water combined with its high termination rate coefficient, usually follow Smith-Ewart Case II kinetics for a certain range of particle sizes and reaction conditions, namely temperature and initiator concentration. And this behavior was observed for styrene miniemulsion polymerization using the oil soluble initiator azoisobutyronitrile, both through experimental and simulation studies.[27]

The behavior of these polymerizations following Case II kinetics is also confirmed by molecular weight results shown in Table 2, according to which the increase of BPO concentration by a factor of 2 caused a reduction of Mn by the same factor (2). Since for Smith-Ewart Case II kinetics for emulsion polymerizations Mn is inversely proportional to the radical entry rate into polymer particles, which, in turn, is directly proportional to the initiator concentration.[28] In addition, average particle diameters (Dp) showed a small decrease during all polymerizations and no noteworthy effect of the BPO concentration on Dp could be observed.

When the reaction rates of the runs with the same BPO concentration are compared it is possible to see a similar behavior for both BPO concentrations, higher conversion and lower Dp in reactions HD than in reactions OTC and HEP. Besides, conversion and Dp show almost the same values between the reactions with n-octane and n-heptane (OCT1/HEP1 and OCT2/HEP2) indicating that there is no considerable difference between the effects of these two low molecular weight alkanes.

Furthermore, for the reactions with these low molecular weight alkanes, the reaction rate is lower than in the reactions with only HD due to their partial solubility in water (Table 3) and the plasticizing effect. The partial solubility in water of these alkanes may favor diffusional degradation and consequently make large particles grow even larger, resulting in an increase of Dp right after the miniemulsification step that leads to a decrease in reaction rate, since the effect of radical compartmentalization decreases with the increase of the particle size.[27,29,30] The plasticizing effect of low molecular weight alkanes was already reported by Villalobos and co-workers[31] who evaluated the influence of n-pentane concentration on the reaction rate of styrene bulk polymerizations. The presence of n-pentane from the beginning of the reaction was responsible for the decrease in the reaction rate and, sometimes, leading to limiting conversions. In the present study, this effect seems also to delay/decrease the gel effect (Figure 2) and add a dilution effect on monomers.

Interestingly the average values (Table 2) and the distribution curves (Figure 3) of the

Table 3.
Aqueous solubility of alkanes used in the styrene miniemulsion polymerizations.[32]

Compound	Solubility (g/100 g H_2O)
N-hexadecane	Insoluble
N-octane	0.002 (at 16°C)
N-heptane	0.005 (at 15°C)

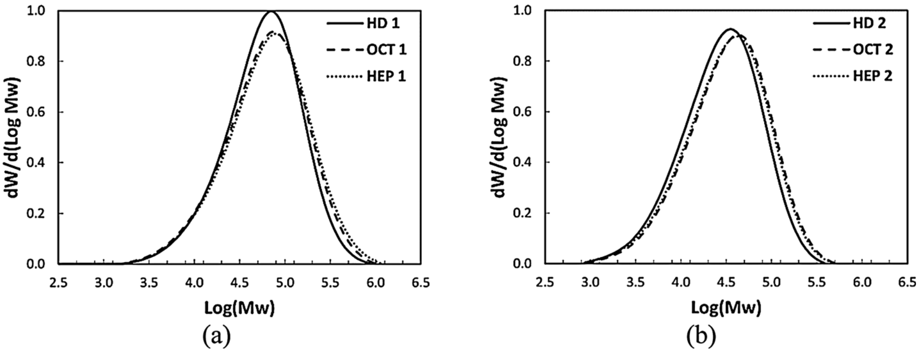


Figure 3.
Comparison between the normalized differential molecular weight distributions of the polymers obtained with different alkane types and 1 mol% (a) and 2 mol% (b) of BPO.

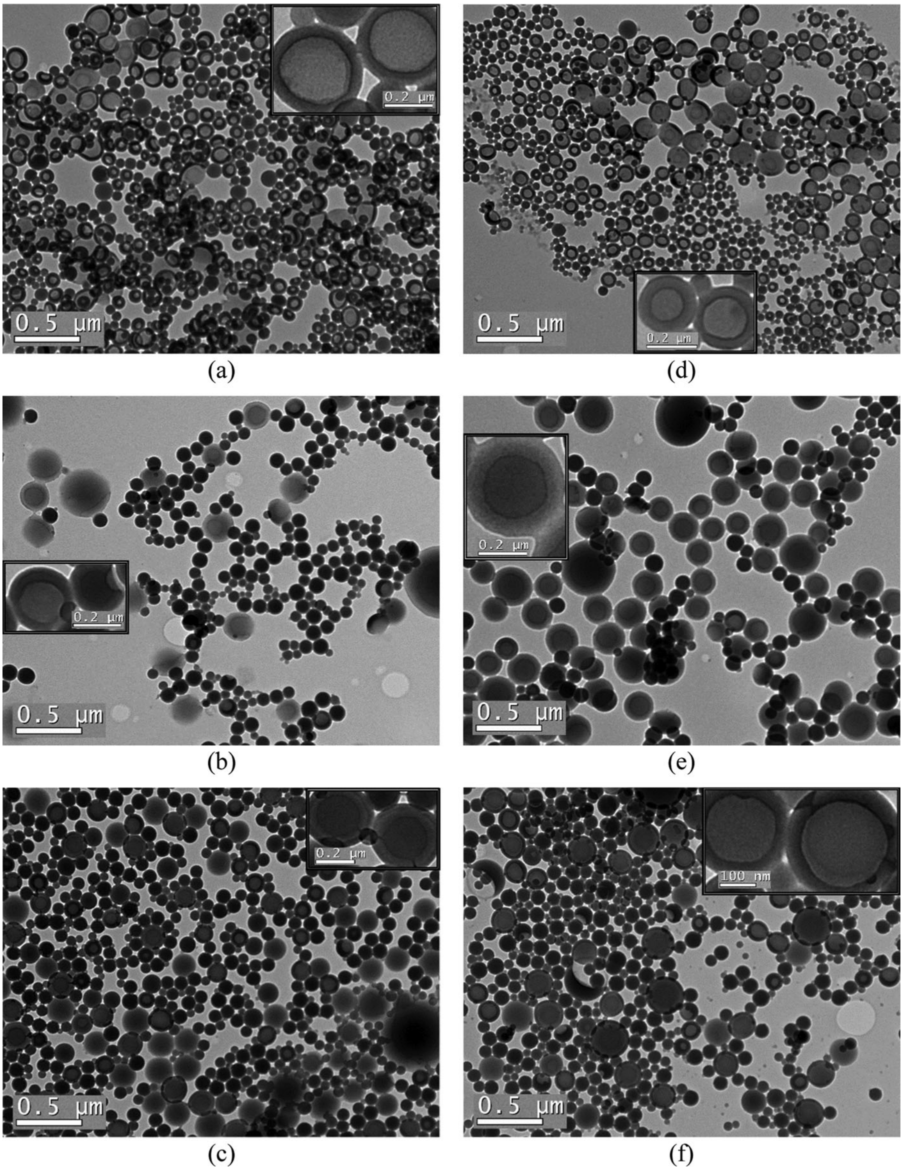
polymers molecular weight using the same BPO concentration and different alkane types do not show remarkable differences, despite their effect on reaction rate and miniemulsion stability. However, in the reactions with higher BPO concentrations the molecular weight distributions were shifted towards lower molecular weights. This is an expected behavior since the increase in the radical generation rate increases the encounter of radicals and the termination reaction frequency, leading to the formation of smaller polymer chains.

TEM micrographs of the final polymer particles obtained in reactions with different alkane types and initiator concentrations are shown in Figure 4. Sequence (a), (b) and (c) corresponding to reactions HD1, OCT1 and HEP1, and sequence (d), (e) and (f) corresponding to the reactions HD2, OCT2 and HEP2, respectively. It is possible to see in these images that all cases show the formation of core-shell particles, however, the quantity and quality of these particles is not the same. In the reactions in which n-octane or n-heptane are used, the number of core-shell particles is smaller and most of the core-shell particles present a less sharp core than the core-shell particles with only HD. As suggested before, it is likely that the phase segregation takes place earlier in cases with only HD due to the higher interfacial tension polymer/HD and higher conversion achieved by these reactions. The BPO concentrations evaluated did not affect significantly the core-shell formation.

Conclusion

Core-shell nanoparticles with a core of different types of alkanes were obtained by miniemulsion polymerization. Two different initiator (BPO) concentrations and three different alkane types were used in the styrene polymerizations. The BPO concentrations evaluated did not affect nanoparticles size and morphology but the other variables. After 30% of conversion the increase of BPO amount led to higher reaction rates due to increase of the number of radicals per particles. In addition, the increase of BPO concentration by a factor of 2 caused a reduction of Mn by the same factor.

Reactions with n-octane and n-heptane and same BPO concentration showed similar behavior between them, resulting in lower reaction rates and higher Dp when compared with reactions with HD only. Also, the reactions with the low molecular weight alkanes showed a lower number of core-shell particles in the TEM images and particle morphology was less sharp. These results were assigned to the plasticizing effect and partial water-solubility of



(a) (d)

(b) (e)

(c) (f)

Figure 4.
TEM images of particles with 1 mol% [(a), (b) and (c)] and 2 mol% [(d), (e) and (f)] of BPO of reactions with HD, n-octane and n-heptane, respectively.

n-octane and n-heptane, responsible for decreasing the gel effect and favoring the diffusional degradation.

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