DOI: 10.1002/masy.201100241

Styrene Miniemulsion Polymerization: Incorporation of N-Alkanes

Claudia A. Capeletto, Claudia Sayer, Pedro H. H. de Araújo*

Summary: In this work, the incorporation of alkane hydrocarbons in poly(styrene-co-methacrylic acid) particles via miniemulsion polymerization was investigated. The reactions were performed at 80 °C for 4 hours, using benzoyl peroxide as oil-soluble initiator. The effects of different concentrations of a hydrophilic co-monomer (methacrylic acid) and different types and concentrations of alkanes, namely n-hexadecane, n-octane and n-heptane were evaluated. Miniemulsion stability at room temperature and reaction kinetics were monitored, as well as the particles size and morphology. Results show the viability of encapsulation of alkanes in miniemulsion polymerizations, especially of alkanes with intermediate chain lengths (e.g. n-hexadecane). When short chain alkanes are incorporated the miniemulsions become less stable, due to their lower hydrophobicity. Based on monomer droplet size distribution data, it was determined that the best concentration of hydrophilic co-monomer for the studied system was 1.0 wt%.

Keywords: alkanes; hydrophilic co-monomer; kinetics (polym.); miniemulsion stability; radical polymerization

Introduction

Miniemulsions are aqueous dispersions of oil droplets relatively stable, with diameter between 50 to 500 nm, prepared from a system containing monomer, water, surfactant and co-stabilizer (highly water insoluble compounds to minimize the diffusional degradation). Since most of the part of the surfactant is adsorbed on the submicrometric droplets surface, particle nucleation occurs primarily by the droplet nucleation mechanism, fact that offers advantages to the incorporation of hydrophobic compounds.[1–3] This fact has led several authors to report in recent years the formation of nanocapsules via miniemulsion polymerization by the use of large amounts of co-stabilizer or other hydrophobic liquids.[4–10]

Incorporation of a liquid core into polymeric shell may cover several purposes, including drug encapsulation for medical use, healing agents for repair methods and volatile liquids for the formation of hollow particles.[11–13] The addition of hollow latex particles in architectural coatings contributes to the opacity of organic films and reduces the required amounts of titanium dioxide and extender pigments in a paint formulation, as well as increasing the abrasion and wet scrub resistance of the films. In paper coatings, their deformation properties influence the gloss of the coated sheet and also reduce the density of the coating formulation. The hollow particles may be obtained by different techniques such as osmotic or solvent swelling, water in oil in water emulsion methods, incorporation of a blowing agent, among others.[14]

The technique of the incorporation of a blowing agent and subsequent expansion is largely employed in industry to obtain expandable polystyrene (EPS), however, there are few reports of its use to obtain submicrometric hollow particles.[15] Moreover, incorporation by this technique

---

Universidade Federal de Santa Catarina - UFSC, Florianópolis - SC
E-mail: claudia.capeletto@gmail.com

occurs in previously formed particles, providing a limited incorporation of blowing agent. Therefore, the possibility of the incorporation of a blowing agent, a short chain alkane for example, in submicrometric particles by miniemulsion polymerization is very interesting, since it unites the reaction and incorporation processes in one single step. Furthermore, this approach allows adding higher levels of alkanes into the particles when compared to the conventional incorporation process made with the particles already formed.

In the last years some works reporting the synthesis of particles with iso-octane encapsulated were presented,[16–18] but none of these reported the synthesis of submicrometric particles containing n-octane or another short chain alkane with a low boiling temperature, since encapsulation is difficult due to lower hydrophobicity. Therefore, in this work we investigated the incorporation of alkane hydrocarbons in poly(styrene-co-methacrylic acid) particles by miniemulsion polymerization, aiming to obtain submicrometric particles containing different alkane types and concentrations for subsequent expansion. The influence of hydrophilic co-monomer and alkane hydrocarbon concentrations on reaction kinetics and droplets and particle sizes were evaluated.

Experimental Part

Materials

Styrene (Sty – 99.6%, Innova S.A.) was used as main monomer, methacrylic acid (MAA – P.A., BASF) as hydrophilic co-monomer, sodium lauryl sulfate (SLS – P.A., Vetec Química Fina LTDA) as surfactant, n-hexadecane (HD – P.A., Vetec Química Fina LTDA) as co-stabilizer and benzoyl peroxide (BPO – P.A., Sigma-Aldrich S.A.) as initiator. N-octane and n-heptane (both P.A., Vetec Química Fina LTDA) were used as hydrophobic compounds to be incorporated, in addition to HD. All reagents were used as received and distilled water was used as continuous phase.

Formulation

Formulations presented from 20 to 26 wt% of organic phase and 1.0 mol% of BPO on the total amount of monomers (fixed at 6.00 g). The amount of HD used in most of the reactions was 6.0 wt% on the amount of monomers, except for some cases in which higher (15 wt%, 30 wt% and 50 wt% in MS HD cases) and lower (4 wt% in MS OCT4 and MS HEP5) amounts were used. The amount of the low molar mass alkanes was varied from about 5 to 15 wt% for n-octane (MS OCT cases) and 5 to 20 wt% for n-heptane (MS HEP cases), both on the total amount of monomers. The aqueous phase consisted of 25.00 g of distilled water and 1.0 wt% of surfactant in relation to the organic phase. The formulations used in the miniemulsion polymerizations are shown in Table 1.

Procedure

Macroemulsions were prepared in a jacketed glass reactor at 23 °C by magnetic stirring of the aqueous and organic phases (both prepared previously). In sequence, the macroemulsions were sonicated with a ultrasonic probe of 400 W (Ultrasonic Dismembrator 500, Fisher Scientific), with an amplitude of 70% during 1 min to form the respective miniemulsions. Once prepared, the miniemulsions were transferred to glass vials of 12 mL, purged with nitrogen and inserted into a thermostatic bath at 80°C to react for 4 hours. For each sampling point a vial was removed of the thermostatic bath and its contents used for analysis. No agitation inside the vials was used during the reactions due to their small diameters.

Characterization

Conversion along the reaction time was determined by gravimetric analysis. The polymer particles and monomer droplets intensity size distribution (PSD and DSD) and intensity average diameter (Dp and Dd) were determined by Dynamic Light Scattering (DLS – Nanosizer Nano S ZEN1600, Malvern Instruments). For this analysis samples were diluted in water

Table 1.
Formulations used in the miniemulsion polymerizations

Reaction	Amount of the reactants (g)							
	Water	*SLS*	*BPO*	*Sty*	*MAA*	*HD*	*n-oct.*	*n-hep.*
MS MAA0	25.000	0.065	0.140	6.000	–	0.360	–	–
MS MAA1				5.940	0.060			
MS MAA2				5.850	0.150			
MS HD1	25.000	0.065	0.140	5.940	0.060	0.360	–	–
MS HD2		0.070				0.900		
MS HD3		0.079				1.800		
MS HD4		0.091				3.000		
MS OCT0	25.000	0.065	0.140	5.940	0.060	0.360	–	–
MS OCT1		0.068				0.360	0.300	
MS OCT2		0.071				0.360	0.600	
MS OCT3		0.074				0.360	0.900	
MS OCT4		0.067				0.240	0.300	
MS HEP0	25.000	0.065	0.140	5.940	0.060	0.360	–	–
MS HEP1		0.068				0.360		0.300
MS HEP2		0.071				0.360		0.600
MS HEP3		0.074				0.360		0.900
MS HEP4		0.077				0.360		1.200
MS HEP5		0.067				0.240		0.300

Please, note that MS MAA1 = MS HD1 = MS OCT0 = MS HEP0.

saturated with monomer in proportion of 50:2 (v/v). The maximal standard deviation of conversion and Dp data were determined based on duplicate reactions. The number of particles (Np) was calculated based on the organic phase amount, conversion and average particle diameter results. The molecular weight was determined by gel permeation chromatography (GPC – HPLC LC-20A, Shimadzu) in equipment with three columns in series, where the first column detects polymers with molecular weight until 1.5×10^3 g/gmol, the second until 4.0×10^5 g/gmol and the third until 2.0×10^8 g/gmol. The samples were prepared by dilution of 20 mg of dry polymer in 4 mL of the tetrahydrofuran (THF, Vetec Química Fina LTDA) and next, the solutions were filtered in a nylon filter with pore size of 0.45 μm. The molecular weights were determined from a calibration curve based on polystyrene standards with molecular weights ranging between 580 g/gmol and 3.8×10^6 g/gmol. The morphology of submicron polymeric particles 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 latex: water) were 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

In the reactions shown in this work, a hydrophilic co-monomer, MAA, was used to decrease the water-polymer interfacial tension and, thus, favor the encapsulation of hydrophobic compounds by a polymer shell. The Figure 1 shows the effect of different MAA concentrations on the evolution of monomer conversion during styrene miniemulsion polymerizations and on the initial DSD.

For the evaluated MAA concentrations, no noteworthy variations were observed in the evolution of conversion with the increase of the amount of MAA, Figure 1(a), since the difference between the points was very close to the maximum standard deviation for conversion data (0.035). However, variations in the initial DSD can be seen in Figure 1(b), where a broadening may be observed in the main peak of the DSD of miniemulsion MS

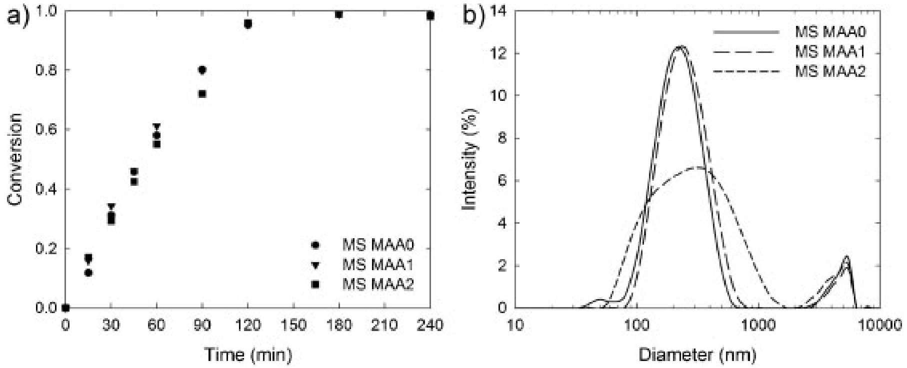

Figure 1.
Effect of MAA concentration on the evolution of conversion during styrene miniemulsion polymerizations (a) and initial intensity droplets size distributions (b).

MAA2, suggesting that the presence of a higher concentration of the hydrophilic co-monomer reduces the stability of the miniemulsion. This might be due to the poorer adsorption of the surfactant on more hydrophilic copolymers, favoring the coagulation of particles.[14] Though it is important to keep in mind that PSDs (and DSDs) determined by DLS must be regarded with care, especially in the case of bimodal distributions, they may be helpful for a qualitative comparative analysis.

The decrease of Dp during the polymerizations, Figure 2(a), which is above the expected due to volume contraction, may be explained by the disappearance of the small peak of big droplets of the initial DSD in Figure 1(b), as observed in the PSD after 30 min and after 240 min of case MS MAA1 in Figure 2(b). This disappearance may be due to monomer diffusion from this bigger droplets to the smaller droplets/particles and/or to the coalescence of these larger monomer droplets until they reach sizes above the reading range of the DLS equipment (0.6 nm to 6.0 μm), both resulting in a decrease of the Dp measured by DLS. Since TEM analysis, Figure 2(c), did not show the presence of particles larger than 1000 nm this second explanation is less probable. When miniemulsion MS MAA1 was maintained at room temperature and without reaction more time was required until the peak of large droplets decreased, though it did not disappear, in the DSD shown in Figure 2(b) after 30 and 240 min. Thus, the Dd of these unreacted miniemulsions remained bigger than the Dp of the respective reactions, as shown in Figure 2(a). Figure 2(d) shows the number size distribution curve of reaction MS MAA1, determined from different images of several regions of the TEM grids to assure representativeness. The particle size range shows a good agreement with that of the intensity distribution determined by DLS (Figure 2(b)), though, as expected, the intensity PSD is more sensitive to the bigger particles than the number distribution, hampering this way a direct comparison of these two different types of distributions. In the same way, the intensity average diameter measured by DLS (146 nm) is bigger than the number average diameter measured from TEM images (122 nm) for reaction MS MAA1.

Based on these results, and in order to favor the incorporation of alkanes, subsequent reactions were conducted with 1.0 wt% of MAA in relation to the total monomer weight (MS MAA1), coinciding with the concentration determined by Luo and Zhou[6] for a styrene/paraffin system.

In the reactions with different amounts of HD, MS HD1 to MS HD4 with 6, 15, 30 and 50 wt% of HD in relation to monomer, the evolution of conversion, shown in Figure 3(a), was influenced by the HD

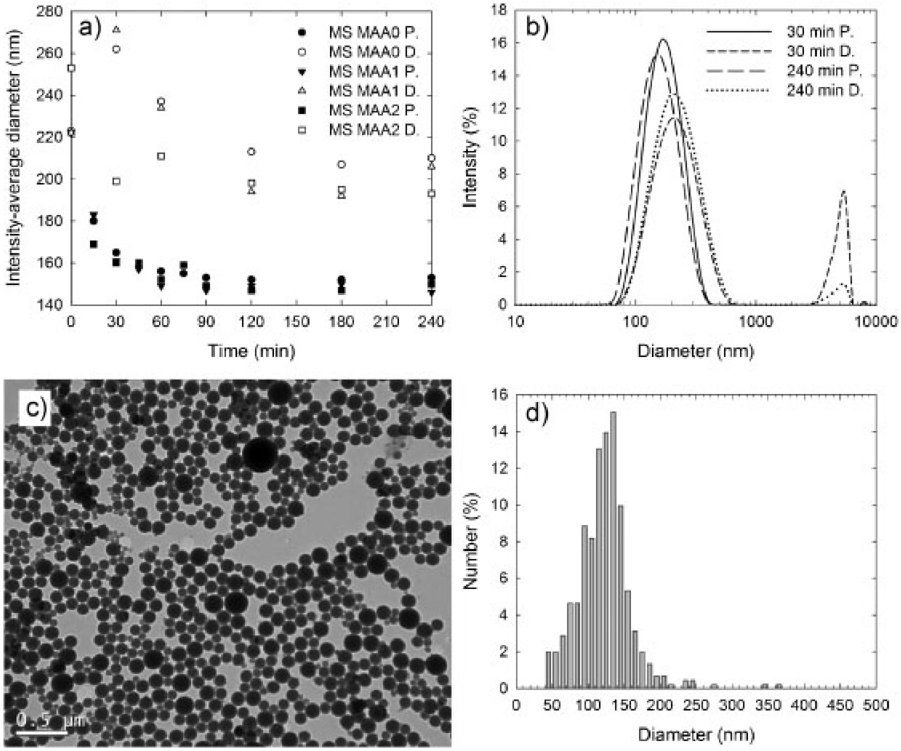

Figure 2.

Effect of MAA concentration on the evolution of average sizes of particles, P., during styrene miniemulsion polymerizations and of droplets, D., of the respective miniemulsions kept at 25 °C without reaction (a); intensity size distributions of particles, P., after 30 and 240 min of reaction MS MAA1 and of droplets, D., of the respective miniemulsions without reaction after 30 and 240 min (b), TEM image of particles of reaction MS MAA1 (c) and number particle size distribution (TEM) of reaction MS MAA1 (d).

amount, as the reaction rate was lower for reactions with higher HD amounts. This difference is largely associated with the dilution effect of the inert component, HD, on monomer and initiator concentrations. In relation to the droplets average diameters, Figure 3(b), case MS HD1 with lowest amount of HD, 6 wt%, presented the largest initial Dd and the Dd of this miniemulsion without reaction varied strongly during the first two hours after minimeulsion preparation. On the other hand, in cases MS HD2 to MS HD4, with higher HD concentrations, the Dd remained rather constant during the evaluated time, 4 h, and were also hardly affected by the amount of HD. This can be explained by the initial DSD shown in Figure 3(c), in which the presence of the second peak (larger droplets population) is observed only in case MS HD1, so miniemulsions of cases MS HD2, MS HD3 and MS HD4 do not have considerably larger monomer droplets. The absence of a second peak for these latter cases may be an indication that the main mechanism involved in the droplets degradation in the studied system is the diffusional degradation, which it is reduced dramatically by increasing of the co-stabilizer concentration. These results are in agreement with those of Casey,[19] who studied the behavior of the droplets and DSD of styrene miniemulsions with HD as co-stabilizer using techniques such as capillary hydrodynamic fractionation (CHDF), acoustic

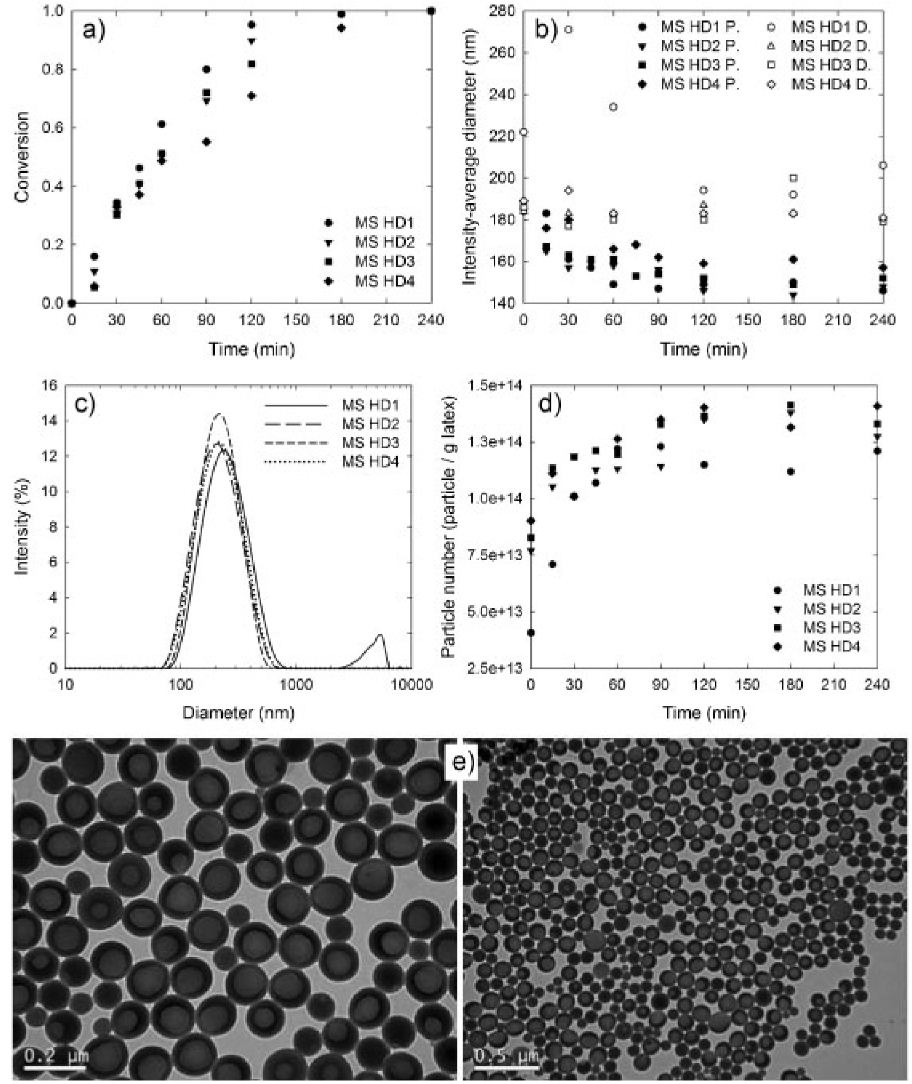

Figure 3.

Effect of HD concentration on the evolution of conversion (a) and of average sizes of particles, P., during styrene miniemulsion polymerizations and of droplets, D., of the respective miniemulsions kept at 25 °C without reaction (b); on initial intensity droplets size distributions (c); on the evolution of particle number (d); TEM image of particles of reaction MS HD4 (e).

attenuation spectroscopy (AAS) and surfactant titration; and also noted the increase of the stability in miniemulsions with higher HD concentrations.

Furthermore, in cases MS HD2 to MS HD4, with higher HD concentrations, the deacrease of Dp during reactions was less pronounced than that of reaction MS HD1, Figure 3(b). The lower decrease in Dp during these polymerizations is attributed to the minimization of mass transfer from larger monomer droplets to smaller droplets/particles with the increase of the HD concentration. In addition, a slight (though greater than the maximum standard deviation, 4.94 nm) increase in Dp was observed with the increase of the HD amount. This increase is atributed to the increase of the fraction of the diperse phase, since the monomer amount was kept constant among these reactions the increase of the HD concentration was reflected in the increase of the fraction of organic phase, from 20 wt% in MS HD1 to 26 wt% in MS HD4. Though the increase of the fraction of organic phase affected mainly the number of polymer particles (instead of their size): $Np_{MS\ HD1} = 1.24 \times 10^{14}$ *per g látex* $< Np_{MS\ HD2} = 1.30 \times 10^{14}$ *per g látex* $< Np_{MS\ HD3} = 1.35 \times 10^{14}$ *per g látex* $< Np_{MS\ HD4} = 1.42 \times 10^{14}$ *per g látex* (Figure 3(d)), since the amount of surfactant was increased with the organic fraction.

The TEM image in Figure 3(e) shows the particles with a nanocapsule morphology, lighter HD core with darker polymer shell,

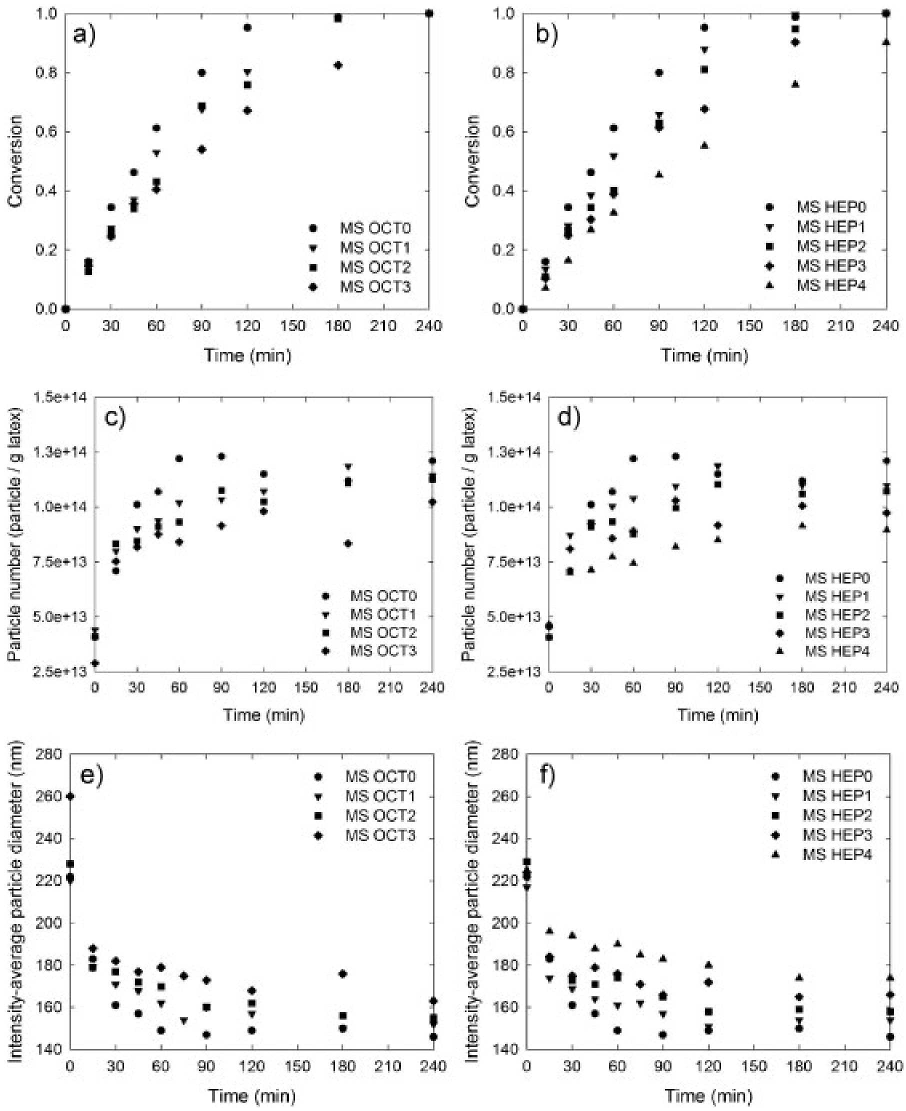

Figure 4.

Effect of n-octane and of n-heptane concentrations on the evolution of conversion during styrene miniemulsion polymerizations MS OCTs (a) and MS HEPs (b), of particle number of reactions MS OCTs (c) and MS HEPs (d) and of intensity-average particles diameters of reactions MS OCTs (e) and MS HEPs (f).

formed in reaction MS HD4 with 50 wt% of HD in relation to monomer. In addition, this high amount of HD resulted in a relatively narrow PSD. Number, weight and intensity average particle sizes based on these TEM images being repspectively, 120 nm, 137 nm and 164 nm. This last value is in good agreement with the intensity average diameter measured by DLS, 157 nm.

For the reactions with the incorporation of 0 to 15 wt% n-octane in relation to monomer (MS OCT0 to MS OCT3) and of 0 to 20 wt% of n-heptane (MS HEP0 to MS HEP4), small increases in the concentrations of these short chain alkanes led to more pronounced reductions of the reaction rate (Figure 4(a) and 4(b)) than in the reactions with increasing amounts of HD (0 to 50 wt% of HD in relation to monomer) in Figure 3(a), due to the dilution effect on monomer and initiator concentrations, and plasticizing effect caused by low molar mass alkanes. Villalobos et al.[20] also observed similar effects when they investigated the influence of n-pentane concentration on the polymerization rate of styrene bulk polymerizations and showed that for reactions with monofunctional initiators the presence of n-pentane from the beginning of the reaction is responsible for the decrease in the reaction rate and, sometimes, led to limiting conversions. Additionally, the decrease in the reaction rate of these reactions is also associated with the decrease of Np with the increase of the short chain alkane concentration, shown in Figure 4(c) and 4(d). This reduction in Np suggests that the increase of Dp, shown in Figure 4(e) and 4(f), is not solely due to the increase of the organic phase fraction, and it is believed that

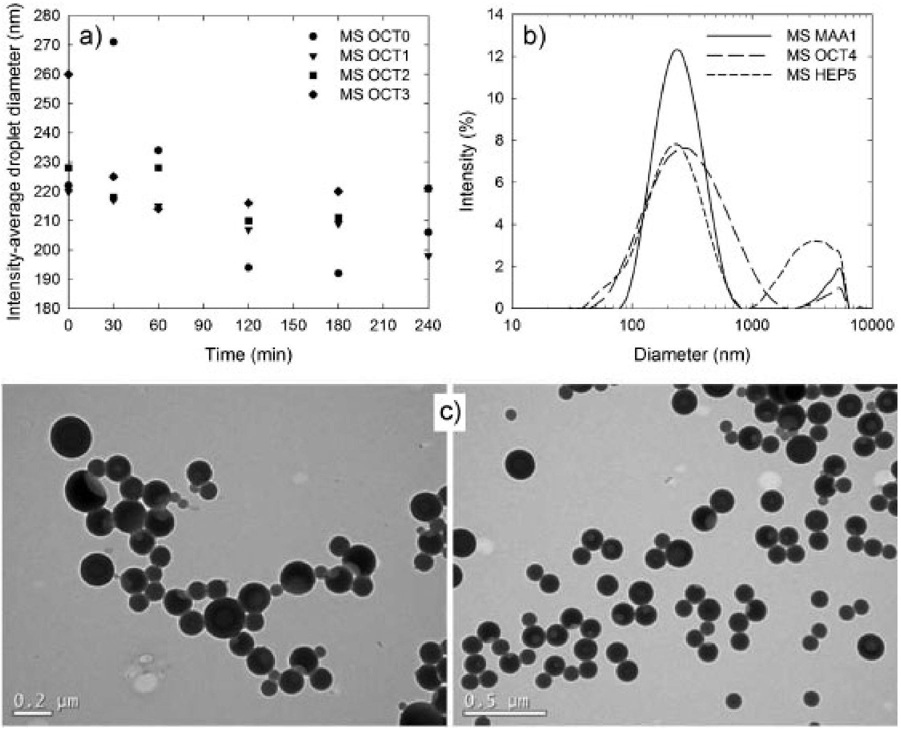

Figure 5.
Evolution of intensity-average droplets diameter of miniemulsions MS OCT's without reaction (a); intensity droplets size distribution at time zero for MS MAA1 (MS OCT0 = MS HEP0), MS OCT4 and MS HEP5 (b) and TEM image of particles of reaction MS HEP4 (c).

the presence of compounds with partial solubility in water (0.002 wt% at 16 °C for n-octane and 0.005 wt% at 15°C for n-heptane),[21] even though much lower than that of styrene, may favor diffusional degradation and, consequently, making large particles grow even larger, resulting in an increase of the intensity average particles diameters measured by DLS.

Figure 5(a) shows the evolution of the Dd of miniemulsions with different amounts of n-octane, except for minimeulsion MS OCT4, which contains only 4.0 wt% of HD in relation to the monomers, all other miniemulsions with n-octane presented similar DSD. Both cases in which the HD concentration was reduced from 6.0 to 4.0 wt% with 5.0 wt% of either n-octane (MS OCT4) or n-heptane (MS HEP5) did not show a satisfactory stability, as can be seen in their initial DSD in Figure 5(b) and a macroscopic phase separation was observed for miniemulsion MS HEP5 30 min after preparation. In the other miniemulsions with n-heptane, but with 6.0 wt% of HD, the evolution of Dd is similar to those of the miniemulsions with n-octane. Figure 5(c) shows a TEM image of particles from reaction MS HEP4 with 6,0 wt% of HD and 20 wt% of n-heptane and a rather satisfatory incorporation of n-heptane may be observed, despite its lower hydrophobicity compared to other compounds, as HD, usually encapsulated via miniemulsion polymerization.

With respect to molecular weight, both average values (Table 2) and the complete distributions (Figure 6), of the polymers with different amounts of HD (Figure 6(a)) and the polymers with different types of alkanes but with substantially the same total amount of alkanes (MS HD2–15 wt% HD; MS OCT2–6 wt% HD and 10 wt% n-octane; MS HEP2–6 wt% HD and 10 wt% n-heptane, Figure 6(b)) didn't show important variations.

Table 2.
Average molecular weight of the different polymers obtained via miniemulsion polymerization

Average molecular weight	Reaction					
	MS HD1	MS HD2	MS HD3	MS HD4	MS OCT2	MS HEP2
Mw	102×10^3	98×10^3	114×10^3	111×10^3	83×10^3	89×10^3
Mn	24×10^3	26×10^3	26×10^3	28×10^3	26×10^3	26×10^3
Mw/Mn	4.2	3.8	4.3	4.0	3.3	3.4

Please, note that MS MAA1 = MS HD1.

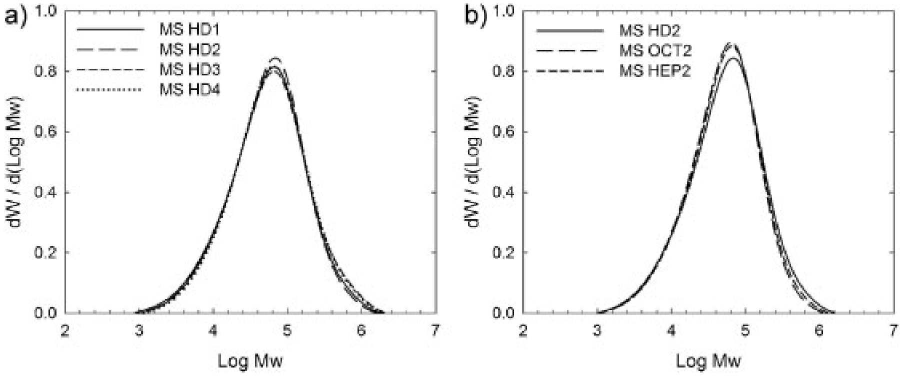

Figure 6.
Comparison between the normalized differential molecular weight distribution curves of the polymers of reactions MS HD's (a) and of reactions MS HD2, MS OCT2 and MS HEP2 (b).

Conclusion

It was observed that under the studied conditions, the presence of 2.5 wt% in relation to monomer of a hydrophilic comonomer (methacrylic acid) can broaden the initial droplet size distribution and, thus, contribute to the reduction of the stability of the miniemulsion. However, the concentration of 1.0 wt% on the total monomer amount favored the incorporation of alkanes (HD, n-octane and n-heptane). Thus, nanocapsules with a HD core and particles with satisfactory incorporation of n-octane and n-heptane were prepared. Effects on reaction kinetics and average particle diameter were observed. The effects on the reaction kinetics are associated with the effects of the monomer and initiator dilution and the plasticizing effect caused by the relatively small molecules of alkanes. The effects on the average diameter are mainly due to diffusional degradation related to the presence of the less hydrophobic short chain alkanes.

Acknowledgements: The authors thank the financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and TEM analysis from Laboratório Central de Microscopia Eletrônica da UFSC (LCME).

[1] F. J. Schork, Y. Luo, W. Smulders, J. P. Russum, A. Butté, K. Fontenot, *Adv. Polym. Sci.* **2005**, *175*, 129–255.

[2] J. M. Asua, *Prg. Polym. Sci.* **2002**, *27*, 1283–1346.

[3] M. Antonietti, K. Landfester, *Prog. Polym. Sci.* **2002**, *27*, 689–757.

[4] F. Tiarks, K. Landfester, M. Antonietti, *Langmuir* **2001**, *17*, 908–918.

[5] A. J. P. Van Zyl, R. D. Sanderson, D. Wet-Roos, B. Klum-Perman, *Macromolecules* **2003**, *36*, 8621–8629.

[6] Y. Luo, X. Zhou, *J. of Polym. Sci.* **2004**, *42*, 2145–2154.

[7] Y. Chen, H. Liu, Z. Zhang, S. Wang, *European Polymer Journal* **2007**, *43*, 2848–2855.

[8] A. P. Romio, N. Bernardy, E. Lemos-Senna, P. H. H. Araújo, C. Sayer, *Materials Science and Engineering: C Materials for Biological Applications* **2008**, *29*, 514–518.

[9] Y. Zhang, S. Zhu, L. Yin, F. Qian, C. Tang, C. Yin, *European Polymer Journal* **2008**, *44*, 1654–1661.

[10] F. R. Steinmacher, N. Bernardy, J. B. Moretto, E. I. Barcelos, P. H. H. Araújo, C. Sayer, *Chem. Eng. & Tech.* **2010**, *33*, 1877–1887.

[11] K. S. Oh, K. E. Lee, S. S. Han, S. H. Cho, D. Kim, S. H. Yuk, *Biomacromolecules* **2005**, *6*, 1062–1067.

[12] B. J. Blaiszik, N. R. Sottos, S. R. White, *Comp. Sci. And Tech.* **2008**, *68*, 978–986.

[13] C. J. McDonald, K. J. Bouck, A. B. Chaput, *Macromolecules* **2000**, *33*, 1593–1605.

[14] C. J. McDonald, M. J. Devon, *Advances in Colloid and Interface Science* **2002**, *99*, 181–213.

[15] H. Ogawa, A. Ito, K. Taki, M. Ohshima, *Journal of Applied Polymer Science* **2007**, *106*, 2825–2830.

[16] A. J. P. Van Zyl, R. F. P. Boscha, J. B. Mcleary, R. D. Sander-Son, B. Klumperman, *Polymer* **2005**, *46*, 3607–3615.

[17] Y. S. Kim, D. Sudol, V. Dimonie, M. El-Aasser, *Key Engineering Materials* **2006**, *306-308*, 1091–1096.

[18] Y. Li, Z. Wang, X. Kong, G. Xue, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2010**, *363*, 141–145.

[19] M. B. Casey, "*Study of Monomer Droplet Behavior in Miniemulsions*", Dissertation of Doctor of Philosophy in Chemical Engineering, Lehigh University, Bethlehem **2009**.

[20] M. A. Villalobos, A. E. Hamielec, P. E. Wood, *J. Appl. Polym. Sci.* **1993**, *50*, 327–342.

[21] R. H. Perry, D. W. Green, J. O'. H. Maloney, "*Perry's Chemical Engineers' Handbook*", 7 rd ed. [S. L.]: Mcgraw-Hill, **1997**.