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Incorporation of PMMA and PS in Styrene and Methyl methacrylate Miniemulsion Homopolymerization

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Summary: In this work, the effect of adding different polymer types, such as polystyrene (PS) and poly(methyl methacrylate) (PMMA), with different molecular weight and variable concentrations on the kinetics and the nucleation mechanisms of styrene and methyl methacrylate miniemulsion homopolymerizations was evaluated. Results showed that higher amounts of predissolved polymer increases the fraction of blend (PMMA and PS) particles formed, indicating that it favors the mechanism of droplet nucleation. However, there is a limit to the incorporation of predissolved polymers as very high viscosities of the organic phase lead to poor dispersion of monomer droplets. It was also noted that other nucleation mechanisms besides monomer droplets nucleation were less important in the miniemulsion homopolymerization of methyl methacrylate than in the styrene homopolymerization.

Keywords: homopolymerization; miniemulsion polymerization; particle size distribution; poly(methyl methacrylate); polystyrene

Introduction

Miniemulsion polymerization has attracted a great deal of attention for the past several years due to the possibility of obtaining new latex materials for many applications being an alternative to conventional emulsion polymerization because in miniemulsion the main mechanism of particle formation is the sub-micron monomer-droplets nucleation. The fact that the *loci* of polymerization is shifted in respect to conventional emulsion polymerization brings special characteristics to latex synthesized from miniemulsions. Incorporation of highly water-insoluble compounds to the polymeric chain or to the polymer particles and alternative control strategies for particle size distribution are among the possible benefits of miniemulsion polymerization.

A miniemulsion is typically formed by intensely mixing an aqueous surfactant solution and an organic phase usually composed of monomer and the costabilizer that is used to reduce the diffusional degradation (Ostwald ripening).[1] Depending on the stabilization system and the mixing process the oil droplets can range between 50 to 500 nm resulting in a very high surface area that allows the droplets to capture the oligomeric water-phase radicals and to become the main loci of polymerization.[2]

Many works were able to show that the use of a low-molecular weight costabilizer, as cetyl alcohol or hexadecane, combined with the presence of low amounts of polymer as the second costabilizer confers greater stability to the miniemulsion.[2–5] This characteristic of the miniemulsion system is quite interesting as it opens the possibility to re-incorporate polymers to latex particles predissolving them in the miniemulsion and to obtain new materials with structured latex particles and with different properties as those of blends of latexes of two homopolymers.

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The type and amount of predissolved polymer added to the miniemulsion dispersion may affect the kinetics and the nucleation mechanism of the miniemulsion polymerization and the properties of the latex particles as its morphology and colloidal stability. Therefore, this work aims to study the effect of the incorporation of different polymers types, such as polystyrene (PS) and poly(methyl methacrylate) (PMMA), with different molecular weights and variable concentrations on the kinetics of styrene and methyl methacrylate miniemulsion homopolymerizations and particle size distribution.

Experimental Part

Materials

Styrene (S, 99.5%, Innova S.A), methyl methacrylate (MMA, 99.5%, ARINOS) were used as received. Hexadecane (HD, 99%) used as costabilizer; sodium lauryl sulfate (SLS, p.a.) used as surfactant; potassium persulfate (KPS, p.a.) used as initiator, were supplied by Vetec Química LTDA, and sodium bicarbonate ($NaHCO_3$) (99%) used as buffer was supplied by Chromate Chemical Products Ltda. Distilled water was used throughout the work. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) synthesized by suspension polymerization were used as predissolved polymers to be incorporated in the miniemulsion reactions.

Formulation and Procedures

The formulations used in the miniemulsion homopolymerizations carried out at constant temperature (70 °C) are presented in Table 1. In all reactions, the polymer, PMMA or PS, was dissolved previously in the monomer for 24 hours at 60 °C using a stirrer speed of 650 rpm. The organic phase was composed of monomer, predissolved polymer and costabilizer (HD), which was added after the complete dissolution of the polymer and mixed for 20 min. The surfactant (SLS) was mixed in water under magnetic agitation for 20 minutes. After that, the organic phase was added to the continuous phase being mixed mechanically for 30 minutes at 1200 rpm. The resulting emulsion was then sonified (Fisher Scientific, Sonic Dismembrator Model 500) at 70% intensity. In the reactions containing polystyrene the ultrasound time was of 8 minutes and for the reactions with poly(methyl methacrylate) this time was increased to 20 minutes due to the higher viscosity of the organic phase. The sonication was carried out in a 50 mL jacketed glass reactor kept at 20 °C. Afterwards, an aqueous solution with sodium bicarbonate and initiator was added and the miniemulsion was distributed in vials (10 cm diameter) that were inserted in a thermostatic bath at 70 °C starting the reaction.

Characterization

The organic phase viscosity was determined using a rotational viscometer (HAAKE

Table 1.
Formulations used in the homopolymerizations (T = 70 °C).

Ingredient	Met 1	Met 2	Met 3	Min 1	Min 2	Min 3	Exp 3	Exp 4
Water (g)	49.93	50.30	50.17	50.09	49.99	50.09	50.91	49.91
SLS (g)	0.238	0.239	0.238	0.239	0.236	0.238	0.236	0.207
KPS (g)	0.034	0.034	0.034	0.036	0.034	0.035	0.033	0.034
$NaHCO_3$ (g)	0.015	0.010	0.013	0.014	0.011	0.012	0.018	0.010
HD (g)	0.470	0.477	0.470	0.476	0.486	0.476	0.477	0.480
Styrene (g)	—	—	—	10.64	10.04	9.43	10.05	—
MMA (g)	10.60	10.08	9.430	—	—	—	—	10
PS (g)	1.18	1.781	2.352	1.18	1.772	2.36	—	—
PMMA (g)	—	—	—	—	—	—	1.776	1.760
% polymer[a]	10	15	20	10	15	20	15	15

[a] wt. % of predissolved polymer related to the monomer + predissolved polymer.

Viscotester 6 L/R plus rotational viscometer). Overall conversions were determined gravimetrically. The average droplet size, the droplet size distribution and the average particle size were measured by dynamic light scattering, DLS (Malvern Instruments Zeta Sizer Nano S) with samples diluted in water saturated with monomer. The number of particles and droplets (Np) was calculated based on the formulation (amounts of co-stabilizer, monomer and polymer) and conversion and average droplet/particle diameter results. Transmission electron microscopy (TEM) (JEOL JEM 1011) at 100 kV was employed to analyze particle morphology and particle size distribution (particles were counted with the software Sizemeter). For this analysis, 1 mL of latex was diluted in 10 mL of distilled water and one drop of diluted latex was poured onto the copper grid with a Formvar film and allowed to dry at room temperature. To increase the contrast between the polymer phases, in some samples PMMA phase was resolved under exposure of a strong electron beam due to preferential degradation of one of the polymer phases as PMMA homopolymers are significantly more beam sensitive than styrenic polymers.[6] Selective etching with ciclohexane was also performed in some samples to extract the polystyrene phase and a thin carbon coating was deposited in these grids by sputter coating to increase the stability of PMMA under the electron beam. The molecular weight distributions were obtained through Gel Permeation Chromatography (GPC) in a Shimadzu - LC 20 AD with RI detector and three columns (GPC 801, 804, and 807). Tetrahydrofuran (THF) was used as eluent at constant flow rate (1.0 ml/min). The molecular weight distributions were determined using polystyrene standards.

Results and Discussion

Figure 1 shows the viscosity of the organic phase as a function of the rotation of the rod for different types and concentrations of polymer. Figure 1a shows that the organic phase with 15 wt.% of PMMA presented a higher viscosity than the organic phase prepared with 15 wt.% of PS as the weight average molecular weight of the PMMA (Mw = 711.7 10^3 g · mol^{-1}) was much higher than of the PS (Mw = 216.5 10^3 g · mol^{-1}). Figure 1b shows that increasing the concentration of polymer in the organic phase the viscosity also increases. The very high viscosity of the solution with 20 wt.% of PMMA resulted in an unfeasible determination of the initial droplet diameter by

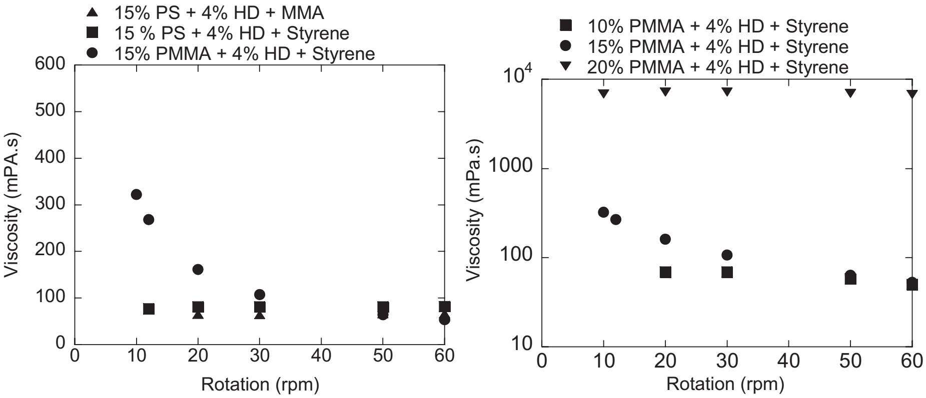
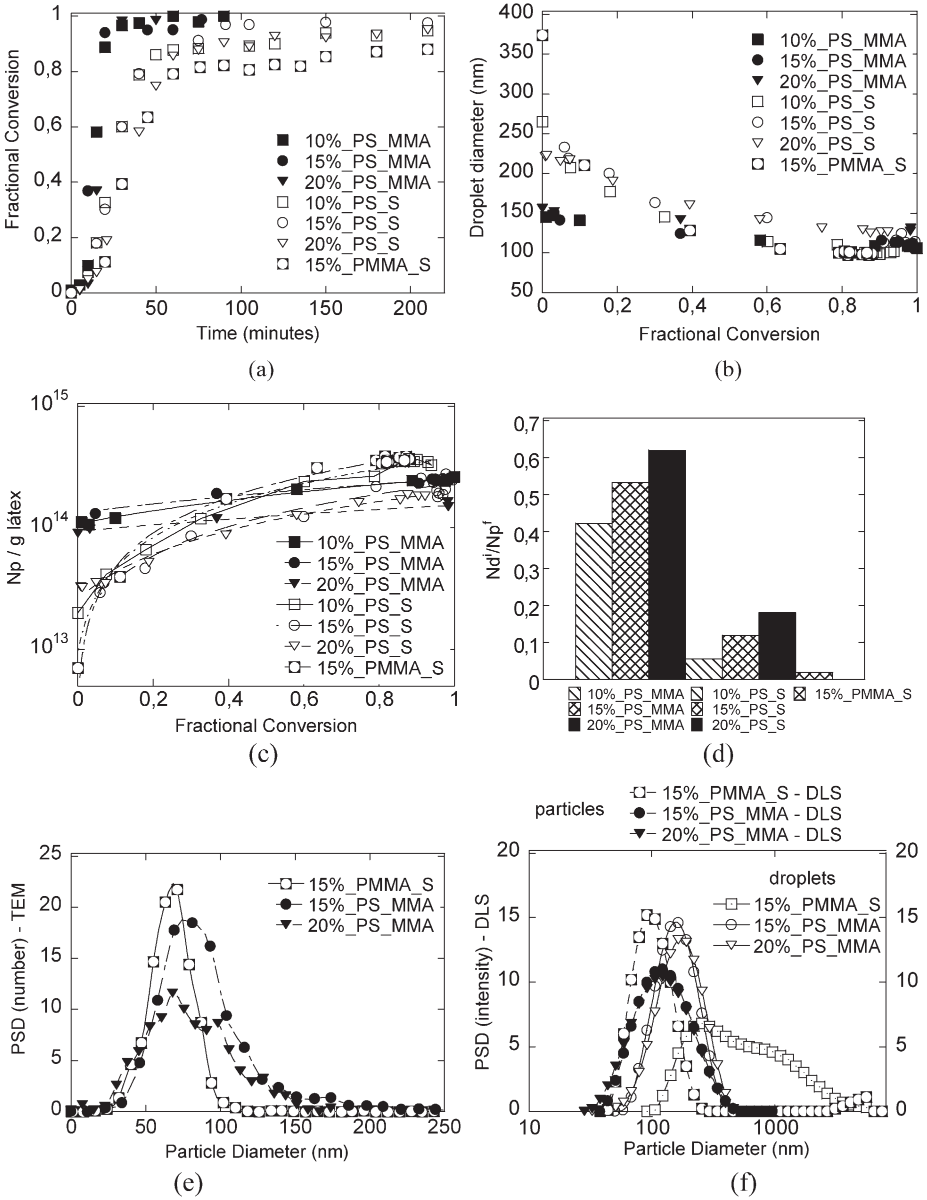


Figure 1.

Viscosity of the organic phase in function of the rotation speed of the rod. Effect of: (a) the types of polymer and monomer and (b) the polymer concentration.

DLS, indicating the formation of an unstable miniemulsion, therefore, the reaction with 20 wt.% of PMMA in the organic phase was not carried through.

Figure 2a shows that the styrene homopolymerization was slower than MMA homopolymerization. This result can be attributed to the higher value of the



(a) (b) (c) (d) (e) (f)

Figure 2.

Evolutions of: (a) conversion; (b) average particles diameter (DLS); (c) and number of particles. (d) number of droplets (N_d^i) and final particles (N_p^f) ratio; (e) final particle size distributions in number (TEM); (f) initial droplets distribution in intensity and final of the particles (DLS). These results were obtained for the homopolymerization of MMA or S in miniemulsion with incorporation of PS or PMMA.

coefficient of the propagation rate of MMA ($k_{pMMA} = 1050$ ($L\,mol^{-1}\,s^{-1}$) at 70 °C [7] and $k_{pS} = 480$ ($L\,mol^{-1}\,s^{-1}$) at 70 °C [8]). In addition, the lower interfacial tension between MMA and the aqueous phase, which favors a better dispersion of the monomer droplets, led to smaller initial average droplet sizes (Figure 2b) and considerably higher numbers of initial monomer droplets (Figure 2c) in the case of the homopolymerization of MMA. This higher number of initial monomer droplets may also have contributed to the faster rate of the MMA polymerization.

During styrene homopolymerizations the average particle size decreased (Figure 2b) and, thus, particle number (calculated assuming uniform particle sizes) increased (Figure 2c). This effect was more pronounced in the reaction with the biggest initial average droplet size (polymerization of styrene with incorporation of PMMA). These results appoint to the presence of other particle nucleation mechanisms in addition to droplet nucleation.

During MMA polymerizations, on the other hand, only a moderate increase in the number of particles was observed. Figure 2d shows the ratio between the initial number of monomer droplets and the final number of polymer particles, N_d^i/N_p^f. It is important to mention, however, that droplets and particle numbers were calculated based on intensity average particle diameters (measured by DLS) assuming that all particles have the same size and, consequently, this ratio N_d^i/N_p^f should not be interpreted as "absolute" values, but only provide some information about the tendency. In this way, this ratio might be regarded as the approximate fraction of polymer particles formed by droplet nucleation and indicates that particle nucleation by other (undesired) mechanisms besides droplet nucleation was less pronounced in MMA homopolymerizations, despite the higher aqueous phase solubility of MMA compared to styrene. This result is attributed to the smaller droplets size of the MMA miniemulsions, which in turn enhances the surface area for radical entry and, hence, droplet nucleation. In addition, droplet nucleation also increased with the amount o PS incorporated.

In the polymerization of styrene with incorporation of 15 wt.% of PMMA, the viscosity of the organic phase was very high (Figure 1a) and, as might be observed in the results shown in Figure 2f, it was not possible to attain a homogeneous dispersion of submicrometric monomer droplets. The relatively large size of the monomer droplets resulted in a smaller as expected total surface area of these monomer droplets and, as a consequence, at the beginning of this reaction surfactant concentration in the aqueous phase was above the CMC (critical micellar concentration) favoring micellar nucleation (surfactant concentration was the kept the same in all reactions, Table 1). In addition, the quite broad distribution of the initial monomer droplets of this reaction may also promote the diffusional degradation of the emulsion reducing further the total surface area of the monomer droplets and releasing more surfactant. When analyzing the final particle size distribution, PSD, for the styrene homopolymerization with 15 wt.% of PMMA, narrow particle size distributions in number (Figure 2e) obtained by TEM and also in intensity obtained by DLS (Figure 2f) are observed. The main reason is the large number of small particles formed either by homogeneous nucleation or by micellar nucleation which shifts the PSD towards lower sizes. In the polymerizations of MMA with the incorporation of 15 and 20 wt.% of PS, on the other hand, due to the predominance of droplet nucleation the final particle size distributions were only slightly broader, as well as slightly shifted towards smaller particles than the respective initial droplet size distributions (Figure 2e and 2f).

Figure 3 presents TEM micrographs of particles formed in the polymerization of styrene with 15 wt.% of PMMA. In these images, the majority of the particles are bellow 100 nm with few large particles

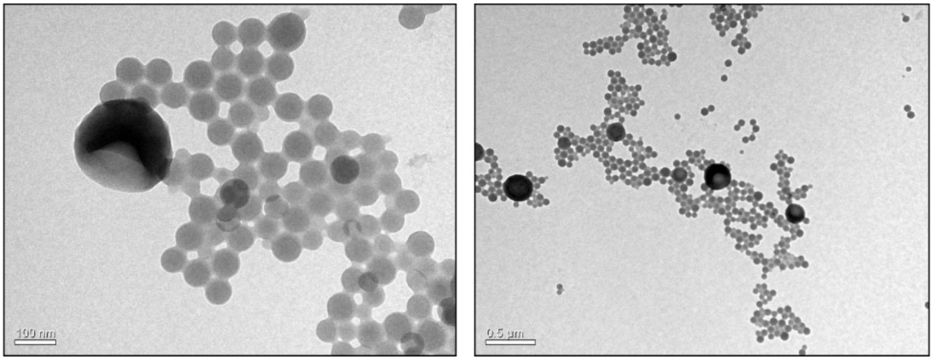


Figure 3.
TEM micrographs of particles synthesized in styrene homopolymerization with 15 wt.% of PMMA.

composed by two different phases (PMMA and PS). As this sample was not recovered with a carbon film, the PMMA present at the large particles degraded partially by the exposure to the strong electron beam of the TEM. Therefore, the darkest regions in these blend particles correspond to PS and the gray regions of these particles correspond to PMMA partially degraded. The particles with lower size (below 100 nm) presented a clear gray color due to the difference in size of the particles, the smaller the clearer, and were composed by PS. This result agrees with the N_d^i/N_p^f ratio presented to Figure 2 (d), where the main mechanism of particle nucleation was not the droplet nucleation. Therefore, just few particles contained the predissolved PMMA and most part of them were composed by pure PS particles formed by micellar and/or homogeneous nucleation.

Figure 4 shows particles formed in MMA homopolymerization with 20 wt.% of PS. To observe the different phases, selective etching with ciclohexane was performed to extract the polystyrene phase and a thin carbon coating was deposited in these grids by sputter coating to increase the stability of PMMA under the electron beam. Therefore the PMMA appears darker than PS. In Figure 4 a high fraction of blend particles can be observed. Counting 578 particles it was determined that 62% were composed of both polymers, this result is in accordance with the N_g^i/N_p^f ratio presented in Figure 2d, once the particles that were nucleated by other mechanisms

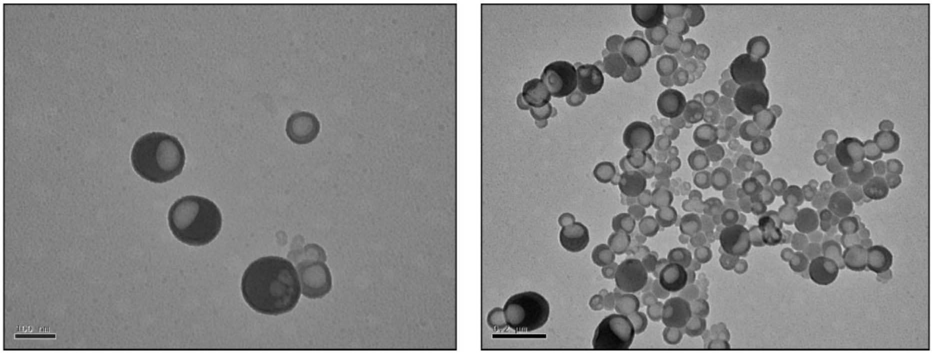


Figure 4.
TEM micrographs of particles synthesized in MMA homopolymerization with 20 wt.% of PS.

than droplet nucleation, cannot be composed of the two types of polymer.

Another aspect to be observed in Figure 4 is that several particles present multiple occlusions. As the MMA reactions were very fast (above 90% conversion was reached in 30 minutes) the equilibrium morphology[11] was not necessarily reached. Additionally, it can be observed that, as presented in Figure 2e, the particle size distribution of this reaction is relatively broad, but even most of the small particles (with diameters below 100 nm) are composed of both homopolymers indicating that they were formed by droplet nucleation.

Conclusion

Results indicated that the predominant nucleation mechanism (droplet, micellar or homogeneous) and, consequently, the fraction of blend particles synthesized depends on the monomer type, styrene or methyl methacrylate, predissolved polymer concentration and its molecular weight. Higher amounts of predissolved polymer increases the fraction of blend particles formed, indicating that it favors the mechanism of droplets nucleation, whereas micellar or homogeneous nucleation mechanisms do not result in the formation of blend particles as the diffusion of the predissolved polymer from the monomer droplets to the aqueous phase is negligible. The higher droplet nucleation is probably due to an effect of swelling of the monomer droplets reducing the concentration of monomer in the aqueous phase. However, there is a limit to the incorporation of predissolved polymers as very high viscosities of the organic phase lead to poor dispersion of monomer droplets.

It was also noted that other nucleation mechanisms besides monomer droplet nucleation were less important in the miniemulsion homopolymerization of methyl methacrylate than in the styrene homopolymerization. This result is attributed to the smaller initial size of monomer droplets in methyl methacrylate miniemulsion polymerization due to the lower interfacial tension between the MMA droplets and the aqueous phase when compared to styrene droplets.

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