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Preparation of PLLA/PMMA and PLLA/PS binary blend nanoparticles by incorporation of PLLA in methyl methacrylate or styrene miniemulsion homopolymerization

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Abstract

Miniemulsion homopolymerization reactions of methyl methacrylate (MMA) and styrene (STY) using poly(L-lactide) as co-stabilizer were carried out in order to prepare poly(L-lactide)/poly(methyl methacrylate) (PLLA/PMMA) and poly(L-lactide)/polystyrene (PLLA/PS) binary blend nanoparticles. The effect of PLLA concentration on methyl methacrylate (MMA) and styrene (STY) homopolymerization reactions was evaluated. It was found that the incorporation of PLLA resulted on acceleration of MMA and STY homopolymerization reactions and led to a molar mass increase of up to 70% for PS in PLLA/PS blend nanoparticles in relation to those prepared without PLLA, which can be attributed to an increase of reaction loci viscosity (gel effect). PLLA also acted as an efficient co-stabilizer, since it was able to retard diffusional degradation of droplets when no other kind of co-stabilizer was used. Two isolated T_gs were found in both PLLA/PMMA and PLLA/PS blend nanoparticles which can be associated to blend immiscibility. TEM images corroborate these results, suggesting that immiscible PLLA/PMMA and PLLA/PS blend nanoparticles could be formed with two segregated phases and core-shell morphology.

Keywords: *miniemulsion polymerization, PLLA, polymer blend, polymeric nanoparticles.*

1. Introduction

Bio-based polymers, either synthetic or natural, have been widely used for a variety of applications, especially in the nanotechnology field due to the large range of applications that biopolymer nanoparticles find in biomedical, agricultural, pharmaceutical, chemistry and packaging areas, not only because of their biodegradability, but also because they are produced from renewable resources[1-6]. Despite that, biopolymers such as polylactide (PLA) still face some application restrictions due to their poor mechanical and thermal properties, high crystallinity as well as poor processability and high cost when compared to petroleum-based polymers[6-8].

Among various methods that can be used to enhance these biomaterials properties, polymer blending with petroleum-based polymers has been considered a promising and cost-effective way to overcome these problems. Also, blending can improve specific polymer properties by providing part of the biopolymers biofuncionality and easy processability of synthetic polymers to the final product[5,6,9,10]. Blending pre-made polymers allows assembling in the final material certain combinations of desired properties exhibited individually by the homopolymers. The final properties of polymer blends depend not only on the chemical composition of the blend but are also strongly influenced by the processing conditions to obtain the blend, the rheological properties and intermolecular interactions of the components[11-13].

Miniemulsion polymerization technique allows blend nanoparticles preparation by polymerization of a monomer in the presence of another polymer in a simple and effective way. Incorporation of highly water-insoluble compounds to the polymeric chain or to the polymer particles are among the possible benefits of miniemulsion polymerization, since the main mechanism of particle formation is the sub-micron monomer-droplets nucleation, thus minimizing secondary nucleation and mass transport through the aqueous phase. However, the blend ratio (monomer:polymer) of nanoparticles prepared by this technique is dependent on the solubility of the polymer on the monomer and the viscosity of this mixture[14-16]. Furthermore, the kinetics and the nucleation mechanism of the miniemulsion polymerization, as well as some properties of the final particles such as its morphology and colloidal stability, may be affected by the type and amount of predissolved polymer added to the miniemulsion dispersion[15].

The objective of this work was to compare MMA and STY miniemulsion homopolymerization using PLLA as co-stabilizer in order to obtain PLLA/PMMA and PLLA/PS binary blend nanoparticles. The effect of PLLA incorporation on polymerization kinetics, molar mass distribution and morphological characteristics of blend nanoparticles was evaluated.

2. Experimental

2.1 Materials

L-lactide (Purac) and Tin II octanoate (Sigma-Aldrich), methanol (Vetec) and chloroform (Vetec) were used in the synthesis of poly(L-lactide) (PLLA). In miniemulsion polymerizations, methyl methacrylate (MMA, Arinos Química, 99.5%) and Styrene (STY, Innova S.A., 99.6%) were used as monomer, Lecithin (Alfa Aesar) as surfactant, 2,2-azo-bis-isobutyronitrile (AIBN, Vetec, 98%) and n-Hexadecane (HD, Vetec, P.A.) as co-stabilizer. Distilled water was employed in all experiments. All materials were used as received.

2.2 Synthesis of PLLA

PLLA was synthesized by L-lactide ring opening polymerization according to the method described by Nijenhuis et al.[17] and Hyon et al.[18] with some modifications. Briefly, dimer and catalyst were added in a glass ampoule and then gaseous nitrogen was fed for 40 minutes at atmospheric pressure. The ampoules were sealed and heated in an oil bath at 140°C for 24 hours. After the removal from the oil bath the ampoules were immediately quenched in cold methanol in order to halt polymerization. The Llactide/catalyst molar ratios used were 5,000 $mol_{Llactide}$/ $mol_{catalyst}$ as suggested in the literature[18]. Unreacted dimer was removed by dissolution on chloroform and precipitation in methanol at 10°C. The weight average molar mass and polydispersity index of PLLA was determined by gel permeation chromatography as M_w = 13700 g/mol and IP = 1.608, respectively.

2.3 Preparation of nanoparticles by miniemulsion polymerization

2.3.1 PLLA/PS and PLLA/PMMA blend nanoparticles

The organic phase was prepared by the dissolution of 0.286 g or 0.421 g of PLLA (10 or 15 wt% in relation to monomer content, respectively) and 0.041 g of lecithin in MMA or STY (2.857 or 2.810 g, respectively, for 10 and 15% of PLLA) during 30 min at 80°C under magnetic stirring in a jacketed glass reactor. Subsequently, the temperature was reduced to 64°C and 0.057 g of AIBN was added and mixed for 2 minutes. Then, 30.0 g of distilled water at 60°C was added to the organic phase and the dispersion was stirred for 5 min. The resulting emulsion was then sonicated (Fischer Scientific, Sonic Dismenbrator Model 500) for 3 min at 60% amplitude in a pulsed regime (30 s sonication, 10 s pause). Batch polymerization reactions were carried out in 12 mL glass ampoules filled with 2.5 mL miniemulsion aliquots each immersed in a thermostatic bath at 72°C for 180 min. It was used an amount of monomer in order to obtain a solids content of 10 wt%.

2.3.2 PMMA and PS nanoparticles

The organic phase was prepared by the dissolution of 0.180 g of n-hexadecane, 0.06g of AIBN and 0.039 g of lecithin in 3.0g of MMA or STY at room temperature under magnetic stirring. Then, 30.0 g of distilled water was added to the organic phase and the dispersion was stirred for 5 min. Sonication and polymerization procedures were carried out as described in section 2.3.1.

2.4 Characterization

2.4.1 Average size and size distribution

The intensity average size and polydispersion index of miniemulsion droplets and final polymer nanoparticles were measured by Dynamic Light Scattering (DLS, Zetasizer Nano S, Malvern Instruments). The samples were diluted in water saturated with monomer to avoid monomer diffusion from the droplets and measurements were made at 20°C.

2.4.2 Monomer conversion

Monomer conversion was determined gravimetrically and also by full evaporation headspace gas chromatography (Shimadzu GC-2010AF with a Shimadzu AOC-5000 headspace autosampler). A flame ionization detector at 220°C and a Restek 30m RTX-5 column with a hydrogen carrier gas flow rate of 1.390 mL/min and heat ramp of 20°C/min (starting at 60°C, maintained for 5 min and ending at 220°C, maintained for 2 min) were employed. The headspace operating conditions were 4 min of shaking at 250 rpm and 110°C for sample equilibration.

2.4.3 Gel Permeation Chromatography (GPC)

The polymers molar mass distributions and weight-averages were determined by GPC. The 0.500 wt% polymer solutions (tetrahydrofuran as solvent) were filtered (0.450 μm Nylon filter) and automatically injected (20 μL) using tetrahydrofuran as eluent at 1 mL/min and oven temperature of 35°C. The chromatograph (Shimadzu LC-20A) was equipped with a refraction index detector (RID-10A) and a 300×80mm column set of three columns in series (GPC-801, GPC-804, and GPC-807). The molar masses were calculated using polystyrene as standards in the range between 580 and 3,800,000 g/mol.

2.4.4 Morphology

Transmission electron microscopy (TEM, JEOL JEM-1011 at 100 kV) was used to evaluate the morphology of polymer particles. The samples were prepared by dropping the dispersion with the nanoparticles on a 300 mesh copper grid coated with a parlodium film. Samples were diluted in water at 1:4. After drying at room temperature, samples were coated with a thin carbon film to avoid degradation of the polymers under the electron beam.

2.4.5 Differential Scanning Calorimetry (DSC)

Thermal analysis of the blend nanoparticles was carried out in a Perkin-Elmer Jade DSC calibrated with zinc and indium. Measurements were carried out using approximately 9.000 mg of freeze-dried samples at a heating and cooling rate of 20°C/min under nitrogen at 20 mL/min. Samples were first heated from 0 to 200°C and maintained at this temperature for 1 min in order to eliminate their thermal history. Then they were cooled to 0°C, maintained at this temperature for 1 min and heated again to 200°C. The glass transition temperature (Tg) was recorded as the midpoint of the heat capacity transition.

3. Results and Discussion

The effect of PLLA incorporation on MMA and STY homopolymerization reactions was assessed based on the polymerization kinetics, particle morphology and blend miscibility. Three formulations for each monomer were evaluated: without PLLA, using n-hexadecane as costabilizer in order to produce neat PMMA and PS nanoparticles, and using 10 and 15% of PLLA in relation to monomer content in order to produce PLLA/PMMA and PLLA/PS blend nanoparticles. Further increase of the amount of PLLA was not possible due to the low solubility of PLLA in MMA . The influence of PLLA concentration on the homopolymerization kinetics of MMA and STY, particle size evolution during the reactions and molar mass distributions and weight averages (Mw) of the obtained polymers are presented on Figure 1 and Table 1. In order to reduce the viscosity of the organic phase (mixture

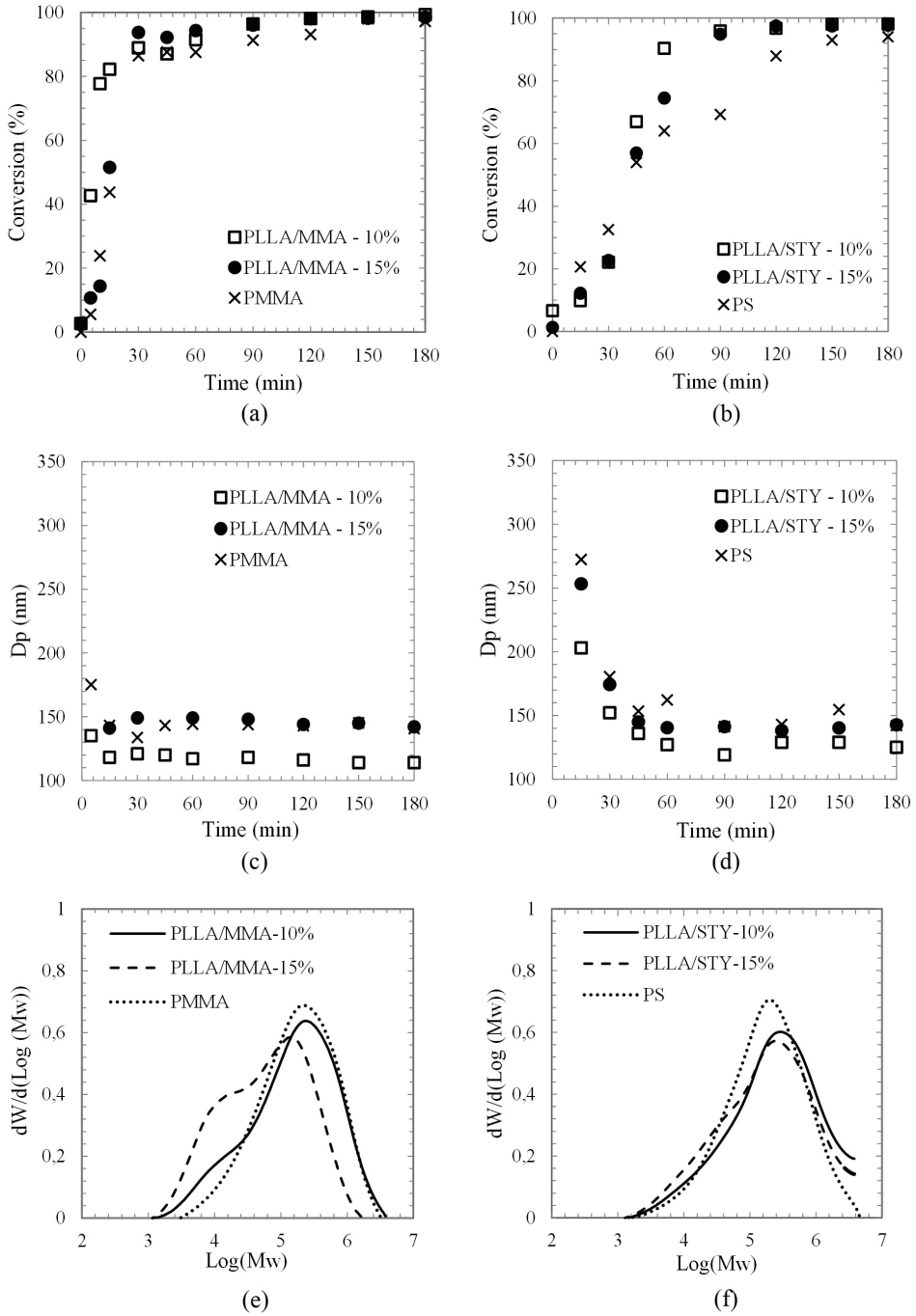

Figure 1. Effect of PLLA content on the evolution of MMA and STY miniemulsion polymerization reactions: (a, b) monomer conversion, (c. d) particle size and (e, f) weight average molar mass distributions.

of monomer and PLLA), the organic phase preparation was performed at high temperature (64-80°C), causing undesired monomer evaporation during this stage. Thus, for monomer conversion calculation, the amount of evaporated monomer was discounted (determined gravimetrically and by gas chromatography).

In Figure 1a and Figure 1b it can be observed that the MMA and STY homopolymerization reactions carried out using PLLA as co-stabilizer were slightly faster than those prepared with n-hexadecane, reaching almost 100% conversion in approximately 90 min. This behavior was stronger for STY polymerization reactions, and is related to a more intense gel effect triggered by PLLA incorporation, which led to an increase of polymerization locus (droplets/particles) viscosity. This phenomenon also affected the molar mass of PS from PLLA/PS blend nanoparticles, as can be seen in Table 1. Blend nanoparticles showed weight average molar mass (Mw) up to 40 to 70% higher than pure PS nanoparticles. Variation on PLLA content (10 and 15%) had no significant effect on STY polymerization rate. For MMA polymerization, on the other hand, an increase of PLLA amount to 15% MMA resulted in a decrease of the initial polymerization rate (first 15 minutes), probably due to a slight increase of the average droplets/particles size (Figure 1c), that reduced the number of particles and thus the total free radical content (compartmentalization effect)[19]. MMA polymerization reactions were slightly faster than those of STY, regardless of PLLA addition. This result can be mainly attributed to a the difference between the propagation rate coefficient of MMA (kp_{MMA} = 1050 L $mol^{-1}s^{-1}$, a 70°C[20]) and STY (kp_{STY} = 480 L $mol^{-1}s^{-1}$, a 70°C[21]), being the latter lower than the half of that from MMA.

The increase of PLLA content led to a slight increase of the average droplets/particles size (Figures 1c, d), probably due to the increase of organic phase viscosity, which turns the dispersion process more difficult. Moreover, despite the higher viscosity of blend droplets/particles, their average size was smaller or equal to those prepared without PLLA (using n-hexadecane as co-stabilizer). These results suggest that PLLA, as well as hexadecane, can efficiently retard difusional degradation of droplets. However, a small decrease of average particle size was observed in the first minutes for all reactions (higher than was expected due to volumetric contraction triggered by the difference of density between monomer and polymer). This behavior can possibly be explained by the co-existence of droplets of different sub-micrometric sizes immediately after sonication. Due to radical compartmentalization, the polymerization rate is higher in the smaller droplets/particles, which results in a monomer concentration gradient that leads to monomer mass transfer from larger to smaller particles[19,22]. This effect is less pronounced in MMA reactions owing to the lower interfacial tension between MMA and the aqueous phase in comparison to STY, which favors a better dispersion of the monomer droplets and led to smaller initial average droplet sizes.

Table 1. Monomer conversion, PS or PMMA weight average molar mass (Mw), polydispersity index (IP), final particle average size (Dp) and polydispersion index (PDI) of polymer obtained.

Reaction	Conversion (%)	Mw (kg/mol)	IP	Dp (nm)	PDI
PMMA	93.1[a]	346	4.9	141	0.067
PMMA/PLLA-10%	99.3[b]	346	8.5	114	0.343
PMMA/PLLA-15%	98.3[b]	141	7.1	142	0.248
PS	94.0[a]	378	6.1	142	0.127
PS/PLLA-10%	98.7[b]	654	11.2	125	0.225
PS/PLLA-15%	98.2[b]	541	12.4	143	0.204

[a] Conversion determined gravimetrically. [b] Conversion determined gravimetrically and by gas chromatography, discounting evaporated monomer.

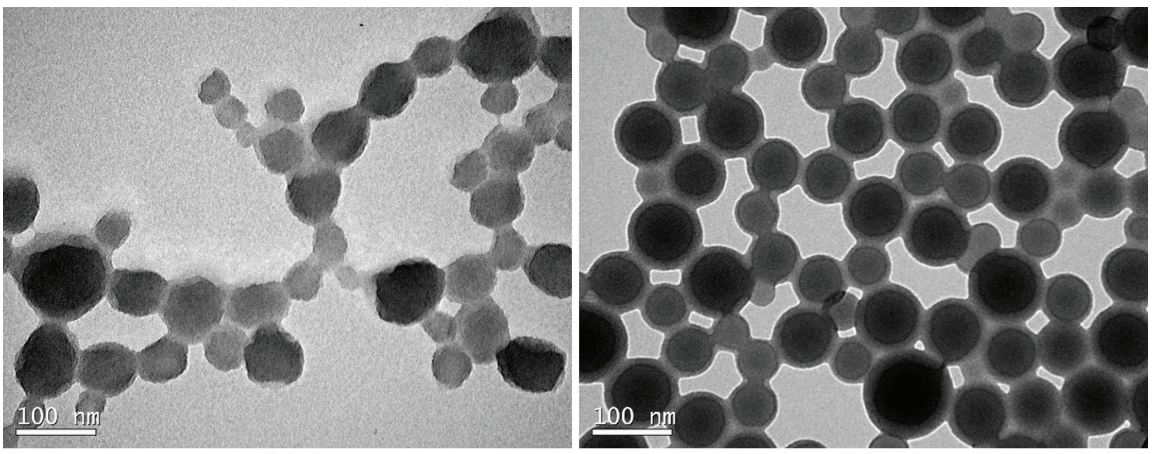

Figure 2. TEM images of blend nanoparticles obtained by miniemulsion polymerization: (a) PLLA/PMMA, with 15% of PLLA, (b) PLLA/PS, with 10% of PLLA.

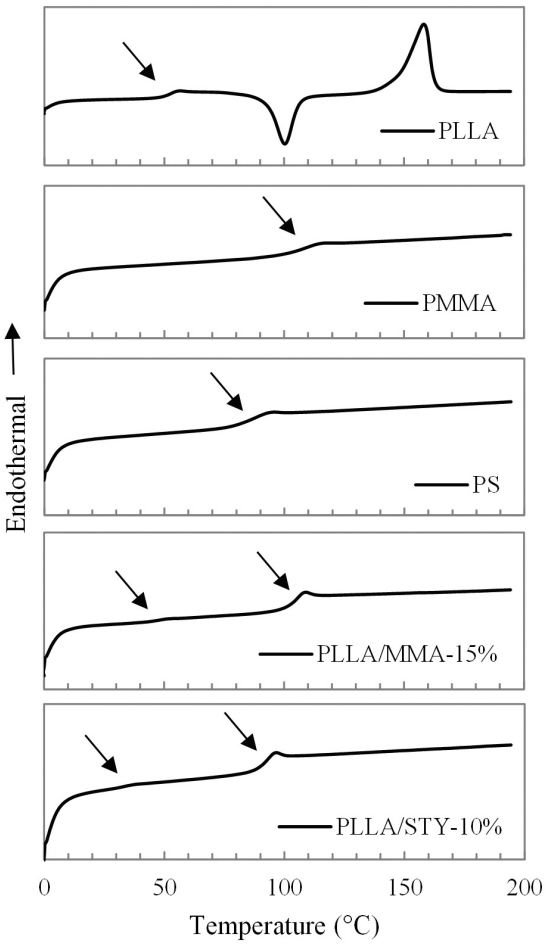

Figure 3. DSC second heating curves of pure PLLA, PMMA and PS and PLLA/PMMA and PLLA/PS blend nanoparticles with 15% and 10% of PLLA, respectively.

The morphology of PLLA/PMMA and PLLA/PS blend nanoparticles with 15% and 10% of PLLA, respectively, can be visualized by the TEM micrographs presented in Figure 2. As can be seen, the miniemulsion polymerization technique was efficient on the preparation of blend nanoparticles. The images suggest that an immiscible blend was obtained, with nanoparticles displaying a core-shell morphology with the more hydrophilic PLLA located outside on the particle and PMMA (Figure 2a) or PS (Figure 2b) in the core.

The glass transition temperature (T_g) of a polymer blend is a common method used to verify the miscibility of polymers. When a single glass transition is found, usually at a temperature intermediate between those of both homopolymers, it is often taken as evidence of the formation of a miscible blend. Polymer immiscibility, on the other hand, is detected by the presence of two T_gs usually with retention of the T_g's values of both individual polymers[11,23]. Figure 3 displays the DSC thermograms obtained in the second heating runs for PLLA, PMMA, PS polymers and PLLA/PMMA and PLLA/PS blend nanoparticles. As can be seen, semi-crystalline PLLA presented an endothermic peak maximum at 158 °C which corresponds to its melting temperature, whereas PMMA and PS are totally amorphous. The endothermic peak of PLLA is no longer detected on blend nanoparticles DSC curves, which may correspond to a decrease of the degree of crystallinity of PLLA and indicates that PMMA and PS molecules restricted the crystallization of PLLA in the blend[9]. In both PLLA/PMMA and PLLA/PS blend nanoparticles samples evaluated, two Tg values close to those of the homopolymers can be observed in each thermogram confirming the formation of an immiscible blend as was already observed on TEM images in Figure 2.

4. Conclusion

It was observed that PLLA can be incorporated on MMA and STY miniemulsion homopolymerization in order to obtain PLLA/PMMA and PLLA/PS blend nanoparticles successfully. As PLLA acted as an efficient co-stabilizer, there was no need to add any other kind of co-stabilizer to retard Ostwald ripening. On the other hand, PLLA incorporation contributed to an increase of reaction rate of both MMA and STY, mainly due to gel effect. As a result there was a significant increase of PS molar mass from the PLLA/PS blend nanoparticles. An increase of PLLA content was followed by a slight increase of the average blend droplets/particles size probably due to the increased viscosity of the organic phase, which turned the sonication process less efficient. TEM images and DSC thermograms indicate the formation of an immiscible blend, with nanoparticles exhibiting a core-shell morphology with the more hydrophilic PLLA located outside on the particle and PMMA or PS in the core.

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