



A novel approach for the synthesis of lactic acid-based polymers in an aqueous dispersed medium

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ABSTRACT

In recent years, the search for environmentally friendly monomers has gradually increased as an important field, attracting the attention of researchers worldwide. Our approach to obtaining lactic acid-based polymers entails the use of an environmentally friendly monomer, derived from lactic acid (ELA), presenting double-bond functionality, allowing it to undergo free-radical polymerization, while further having an eco-friendly water-based miniemulsion polymerization process. It has been demonstrated that the ELA/methyl methacrylate (MMA) copolymer can successfully be synthesized. Highly stable latexes were obtained at high conversion. The incorporation of ELA and its effect on the copolymer properties were evaluated; results indicated that polymer properties such as average molar masses and glass transition temperatures are strongly dependent on the ELA composition.

1. Introduction

The search for new polymeric materials presents an important challenge in the polymer reaction engineering field. In this scenario, lactic acid-based materials play a fundamental role in the development of polymers used for biomedicine, food packaging, and coating applications, among others (Esmaeili et al., 2017; Bajpai et al., 2012; Dusseiler et al., 2013; Singhvi and Gokhale, 2013; Rooney et al., 2017).

Most synthetic polymers are produced from petroleum and synthetic fibers, which can be toxic and non-biodegradable. Such materials depend on non-renewable raw material that require, thus, long degradation periods. Therefore, there is a concern with regard to the development of biodegradable polymers to obtain an ecological product. In this context, lactic acid-based polymers are materials of attention in the scientific area (Hamad et al., 2018; Zubov and Sin, 2018; Yang et al., 2012).

The conventional polymerization methods (e.g. step-growth and ring-opening) used for the synthesis of lactic acid-based polymeric materials can be very complex, exhibiting high energetic cost, high dependence on the type of catalyst used and, additionally, purification steps are needed. Hence, the total cost of the polymerization process is high. Moreover, poly(acid lactic) - PLA presents several disadvantages

which are not limited to: low flexibility, toughness, and limited processability; as a result, its ability to be adjusted for use in several technological applications makes the task challenging (Esmaeili et al., 2017).

One of the major technological challenges related to the sustainable synthesis of polymers concerns the development of efficient production routes that allow the synthesis of polymeric materials under moderate and controlled operating conditions. In this scenario, miniemulsion is regarded as environmentally friendly polymerization processes, since they do not use, as a continuous medium, volatile, environmentally harmful organic compounds and, on the other hand, this polymerization processes allow the use of milder operating conditions with the benefit of reducing energy consumption and controlling the final properties of the polymeric materials. The sustainable development of polymeric materials must necessarily meet process requirements such as: *i*) reduction of thermal energy consumption; *ii*) use of aqueous heterogeneous polymerization systems whose operational characteristics allow for a better control of the process; *iii*) reduction of consumption of raw materials from non-renewable fossil resources; *iv*) increase of chemical reaction efficiency with respect to atomic and mass economy, selectivity and yield; *v*) elimination of toxic, explosive and/or harmful organic solvents that are prejudicial to health, process safety and the

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environment (McElroy et al., 2015; Summerton et al., 2016; Abou-Shahada et al., 2017; Thomsett et al., 2019).

Miniemulsion polymerization is a heterogeneous process capable of producing very stable latexes presenting polymer particles with sizes lying in the interval from 50 nm to 500 nm (Antonietti and Landfester, 2002; Asua, 2002; Schork et al., 2005). This process exhibits several advantages in comparison to classical polymerization systems, such as emulsion and suspension, which can be related to: *i*) the nucleation process taking place directly in the monomer nanodroplets, homogeneously dispersed into the aqueous continuous phase not requiring the presence of micelles in the medium; *ii*) both water-soluble and organo-soluble initiators can be employed in the polymerization; *iii*) polymer materials with narrow particle size distributions are obtained as result of the action of high shear devices such as rotor-stator systems, high-pressure homogenizers or ultrasonic high power systems, which are successfully employed to reduce the monomer droplets size combined to the essential use of hydrophobic agents (N.B. for control of diffusional degradation mechanism τ_1) and surfactants (N. B. for control of coalescence mechanism τ_2). One should keep in mind that due to the large surface as a result of the intensive shear forces, the nucleation of submicron droplets consists of the predominant particle nucleation mechanism, which favors the synthesis of polymeric materials with very distinct features when compared to conventional emulsion polymerization in heterogeneous systems, such as suspension and emulsion polymerizations. Additionally, due to the effective use of surfactant/co-stabilizer system that leads to formation of very stable monomer droplet dispersions, the mass transfer of monomer through the aqueous phase is not required; *iv*) polymer materials with high average molar masses and tailored molar mass distributions can be synthesized; *v*) high potential for the incorporation of substances exhibiting high hydrophobicity. In this particular case, the polymerization of monomers from renewable sources, such as vegetable oils and their derivatives is successfully carried out, even considering that these compounds have low intrinsic reactivity and low solubility in the aqueous continuous medium, which cannot be well performed via classical emulsion polymerization due to the mass-transfer mechanism limitations that affect the diffusion of monomer(s) from the microdroplets through the aqueous phase to the growing polymer particles (Ouzineb et al., 2006; Samer and Schork, 1999; Lauterborn and Ohl, 1997; Mason., 1988, 1994; Landfester et al., 1999; Araujo et al., 2001; Cardoso et al., 2013).

This study aims to focus on the synthesis of a novel polymeric material based on methyl methacrylate (MMA) and esterified lactic acid (ELA) via miniemulsion polymerization process. ELA consists of a macromonomer formed by the esterification of lactic acid and acrylic acid (AA), utilizing methanesulfonic acid as a catalyst, in the presence of hydroquinone to prevent the polymerization of acrylic acid, which resulted in the formation of a new monomer presenting a functionality of double-bonds, allowing free-radical polymerization to take place. Scheme 1 exemplifies the esterification reaction used in the modification of the lactic acid with the acrylic acid.

The use of modified lactic acid as a monomer in polyaddition reaction is very intriguing, because the reaction can be performed under mild reaction conditions in heterogeneous processes, thus lowering the costs of the polymerization process. Moreover, heterogeneous polymerization processes are widely employed to produce large amounts of polymeric materials all over the world, including emulsion, dispersion,

precipitation, suspension and miniemulsion polymerizations (Pinto et al., 2013).

It is well known that the polymerization processes mentioned above present several advantages including relatively easy temperature control, consequently resulting in the easy removal of reaction heat; a possible ability to control macromolecular and morphological properties of the final polymer, achieved adjusting operating conditions during polymerization (Schork et al., 2005; Nomura et al., 2005).

Furthermore, it is noteworthy to emphasize that methyl methacrylate (MMA) has also been used as a comonomer, due to the final properties of MMA-based polymer materials, such as: non-toxicity, low cost, ease of processability, compatibility, minimal tissue inflammatory reactions, and a greater resistance to fracture. These key characteristics give the polymer a gateway for application in the biomedical field (Ali et al., 2015).

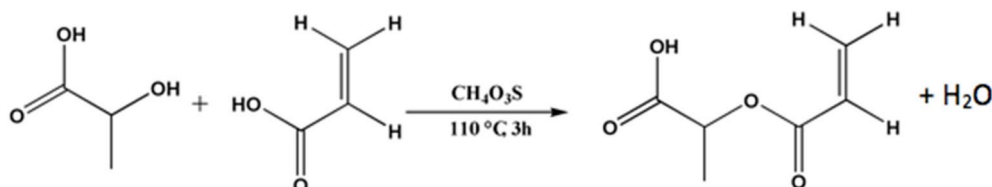
The fundamental objective of this research is to establish an environmentally friendly route to produce polymers from lactic acid-derived acrylated monomer using an aqueous heterogeneous process. It is important to highlight that the modification of lactic acid is carried out with carboxylic acid such as acrylic acid, which can be obtained from renewable sources (Thomsett et al., 2016; Noppalit et al., 2019). To the best of our knowledge, the present study provides inaugural work of the production of lactic acid-based polymers nanoparticles through miniemulsion polymerization. The combination of an aqueous dispersion polymerization process with methyl methacrylate and esterified lactic acid is essential to produce a new class of environmentally friendly polymer materials.

2. Experimental

The selective esterification of lactic acid with acrylic acid was carried out in a 250 mL three-neck round-bottom flask under vigorously stirring, heated in a silicone oil bath. The reaction vessel was equipped with *i*) a hotplate IKA C-MAG HS 7 (IKA Works, Inc.), linked to a Pt1000 temperature probe with an integrated temperature control to maintain the reaction temperature at the setpoint; *ii*) a Dean-Stark apparatus for continuous removal of the water produced during the reaction; *iii*) a funnel for the controlled addition of acrylic acid and methanesulfonic acid.

The monomer (ELA) derived from lactic acid (LA) was synthesized through *D,L*-lactic acid esterification with acrylic acid catalysed by methanesulfonic acid in the presence of hydroquinone to prevent polymerization of acrylic acid, leading to the formation of a new monomer presenting double-bonds functionality, to allow a free-radical polymerization to occur. Initially, 0.2 mol of lactic acid and 0.1 mmol of hydroquinone were added to the round-bottom flask. When the internal temperature of the flask reached 100 °C, 0.2 mol of acrylic acid and 2 mmol of methanesulfonic acid were added dropwise with the aid of the funnel. The system was subjected to vacuum and the reaction was carried out under constant mechanical stirring at 600 rpm for 3 h.

The esterification reaction of lactic acid with acrylic acid was in real-time and in-situ monitored for 3 h via FTIR spectroscopy. FTIR spectra were in-situ collected with the mid-infrared based system, ReactIR 15 equipment (Mettler Toledo Ind. e Com. Ltda), configured to scan the spectral region from 2500 cm^{-1} to 650 cm^{-1} at 8 wavenumber resolution with MCT Detector using Happ-Genzel apodization and DiComp



Scheme 1. Esterification reaction between lactic acid and acrylic acid.

(Diamond) probe connected via AgX 9.5 mm x 2 m Fiber (Silver Halide). The iC IR™ software was used for data acquisition and mathematical treatment with a sampling interval for TFIR scanning equal to 180 s.

Initially, for the preparation of the miniemulsion, the organic phase (containing 0.15 g of hexadecane, 6 g of monomer) and aqueous phase (containing 33 g of water, 0.15 g of sodium dodecyl sulfate, and 0.15 g of initiator of polymerization potassium persulfate, KPS) were prepared under magnetic stirring for 30 min. Subsequently, both the organic and aqueous phases reached a homogenized state under vigorous magnetic stirring for 30 min to form a pre-emulsified system; ultimately the system was subjected to ultrasonication (Cole-Parmer® 750 W ultrasonic processor with temperature controller) for 4 min at 70% amplitude (10 s on/5 off). During the formation of the nanodroplets, the pre-emulsified system was cooled by using an ice bath to avoid early onset of polymerization.

The miniemulsion copolymerization reactions (containing the modified lactic acid monomer – ELA in the range from 0.0 wt% to 20 wt %) were performed in 20 mL glass ampoules, under heating via recirculating water bath at 80 °C for 2 h.

The resulting polymer latex was quenched by the addition of a hydroquinone solution (200 ppm) to inhibit the polymerization of unreacted monomers, followed by drying until constant weight in an oven at 60 °C for 72 h.

The reaction conversion was determined by gravimetric measurements. The latex and polymer samples were characterized by Dynamic Light Scattering (DLS) on a Malvern Zetasizer NanoSeries (model NANO ZS) to determine the average diameter of the nanodroplets and polymer lattices.

Dried polymer samples were characterized by *i*) differential scanning calorimetry (DSC) to determine the glass transition temperature (T_g), which was performed on a Shimadzu DSC-60 calorimeter (Shimadzu Scientific Instruments, Maryland, USA) at heating rates of 10 °C·min⁻¹ with a temperature range of -30 °C–200 °C, under helium atmosphere with a flow rate of 50 mL min⁻¹; *ii*) thermogravimetric analysis (TGA) to evaluate the thermal stability of material, which was carried out on a thermogravimetric analyzer Shimadzu DTG-60H (Shimadzu Scientific Instruments, Maryland, USA) at heating rates of 10 °C·min⁻¹, temperature range from 25 °C to 800 °C, under nitrogen atmosphere with a flow rate of 30 mL min⁻¹; *iii*) gel permeation chromatography (GPC) was performed on a Viscotek GPCmax™ (Malvern Instruments Ltd, Worcestershire, United Kingdom) equipped with inline degasser, pump, oven, autosampler, three linear separation columns (KF-802.5, KF-804L e KF-805L installed in sequence) and refractometer detector. The calibration curve used to determine average molar masses (M_w and M_n) and molar mass dispersity ($D_M = M_w/M_n$) was built using standard polystyrene samples with mass-average molar mass ranging from 1.2·10³ to 4.5·10⁶ g mol⁻¹ and molecular-weight dispersity close to 1.0. GPC measurements were conducted at 40 °C using tetrahydrofuran (THF) as a mobile phase at a flow rate of 1 mL min⁻¹ with an injection loop of 100 µL. The polymer samples were solubilized in THF (0.75 g L⁻¹) and filtered through 0.45 µm PTFE membrane filters prior to analysis; *iv*) ¹H NMR spectroscopy was used for elucidating the structure of the ELA monomer and the composition of the copolymeric materials. The experimental runs were carried out in a Bruker Magneto Ascend 600 MHz, using approximately 20 mg samples, dissolved in 1 mL of deuterated chloroform (CDCl₃) with tetramethylsilane (TMS) as the internal standard; and *v*) X-ray diffraction (XRD) measurements carried out on a Bruker D8 FOCUS X-ray diffractometer (Bruker AXS, Inc., Wisconsin, USA), using CuKα radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV and 30 mA) operating in the angular range $5 \leq 2\theta \leq 80$ with steps of 0.05° at a rate of 0.25°·min⁻¹.

3. Results and discussion

NMR spectroscopy was employed to evaluate the chemical structure of the lactic acid-based monomer synthesized through selective

esterification between the lactic acid and the acrylic acid, leading to a yield of approximately 95%. Fig. 1 shows the spectra obtained at the beginning of the reaction (Fig. 1A) and 3 h after reaction time (Fig. 1B). As depicted in Fig. 1, the double bonds of acrylic acid are indicated by double doublets, represented by the letters c, d and e. The peak at 1.45 ppm represents the hydroxyl of LA, which is the alcohol (hydroxyl functional group) and the esterification reaction site. Apparently, the peak at 2.86 ppm is characteristic of the hydroxyl group of the AA that will make the attack, for the esterification to take place. Therefore, they should be suppressed in the final product, which is indicative that esterification had occurred. The suppression of the hydroxyl peaks in the final product is an indication of the successful esterification reaction (N. B. ¹³C NMR spectrum of lactic acid-derived acrylate monomer is shown in Fig. S1 in the supplementary material).

FTIR spectra of reaction medium along the time were acquired, as illustrated in Fig. 2. It can be noticed that significant spectral changes take place along the batch reaction, indicating that this real-time, in situ mid-infrared technique can be successfully employed to study the esterification reaction progression. Fig. 2B shows the deconvolution of the infrared spectra of the reactants (purple, related to the beginning of the reaction) and the product (red, associated to the end of the reaction). It can be observed the appearance of a signal at 1096 cm⁻¹ in the spectrum of products is characteristic of ester C–O stretching, which is an indication that esterification has occurred. Another indication is the suppression of the signal at 1126 cm⁻¹ in the characteristic C–O reactant spectrum of alcohol, showing that the hydroxyl of lactic acid was consumed during the reaction. In 1730 cm⁻¹, it is still possible to verify the stretching of the pair referring to carbonyl. The double bond between the carbons can be verified on the signals at 1630 cm⁻¹.

As the copolymerization of the new monomer derived from LA is intended to take place in dispersed mediums such as a miniemulsion system through free-radical polymerization, it is very important to maintain double-bonds functionality. According to Fig. 1, LA was successfully esterified with AA, leading to the formation of a monomer and presenting a reactive functional group capable of undergoing radical chain polymerization.

Fig. 3 shows the NMR spectra of the ELA/MMA polymers synthesized with feed ELA composition lying in the interval from 0 to 20 wt%. The first one (Fig. 3A) refers to the MMA homopolymer, which served as reference. Spectral changes were observed as the concentration of ELA was increased in the organic phase. The molar fraction of ELA incorporated in the copolymer chains was determined based on Equation (1) and is presented in Table 1 (Jensen et al., 2016; Eren and Küsefoğlu, 2004).

$$\chi_{ELA} = \frac{N_a I_{H_b}}{N_a I_{H_b} + N_b I_{H_a}} \quad (1)$$

where χ_{ELA} corresponds to the molar fraction of ELA in the copolymers, I_{H_b} is the integral value concerning the peak marked with the letter (b) (related to ELA monomer) in the molecular structure of Fig. 3; I_{H_a} is the integral value regarding the peak marked with the letter (a) (associated with MMA monomer) in the molecular structure in Fig. 3; N_a is the number of protons related to the peak (a) and N_b is the number of protons related to the peak (b).

It is well known that the final properties of the polymeric materials are closely related to the chemical composition, sequence of repeated units and tacticity. In the particular case of ELA/MMA copolymers, the steric arrangement of the copolymer chains based on ¹H NMR spectrum, depicted in Fig. S1 of the supplementary material, strongly depends on the hydrogens of the polymeric chains associated with the protons of the methyl group (-CH₃), characterized by the chemical shifts in approximately 1.21, 1.02 and 0.84 ppm, related to isotactic (mm), atactic (mr) and syndiotactic (rr) triads, respectively (Aguilar et al., 2011; Dion et al., 2010; Juliete et al., 2017). According to Table S1 in the supplementary material, the ELA/MMA copolymers consist of around 4% isotactic, 36%

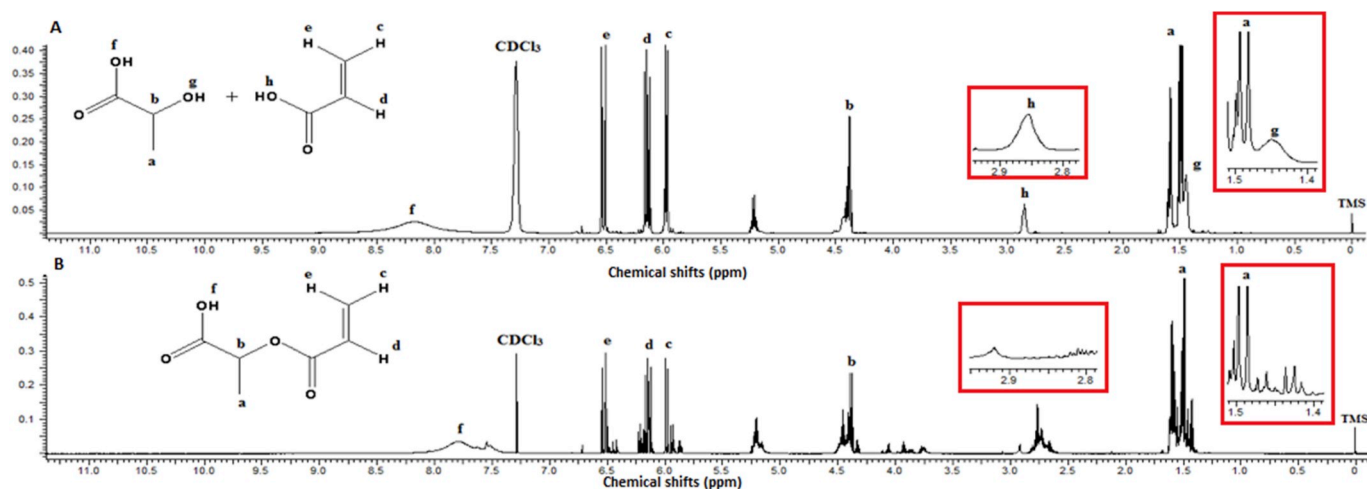


Fig. 1. ¹H NMR spectrum related to the esterification reaction medium containing lactic acid and acrylic acid. (A) Initial reaction medium and (B) Final reaction medium.

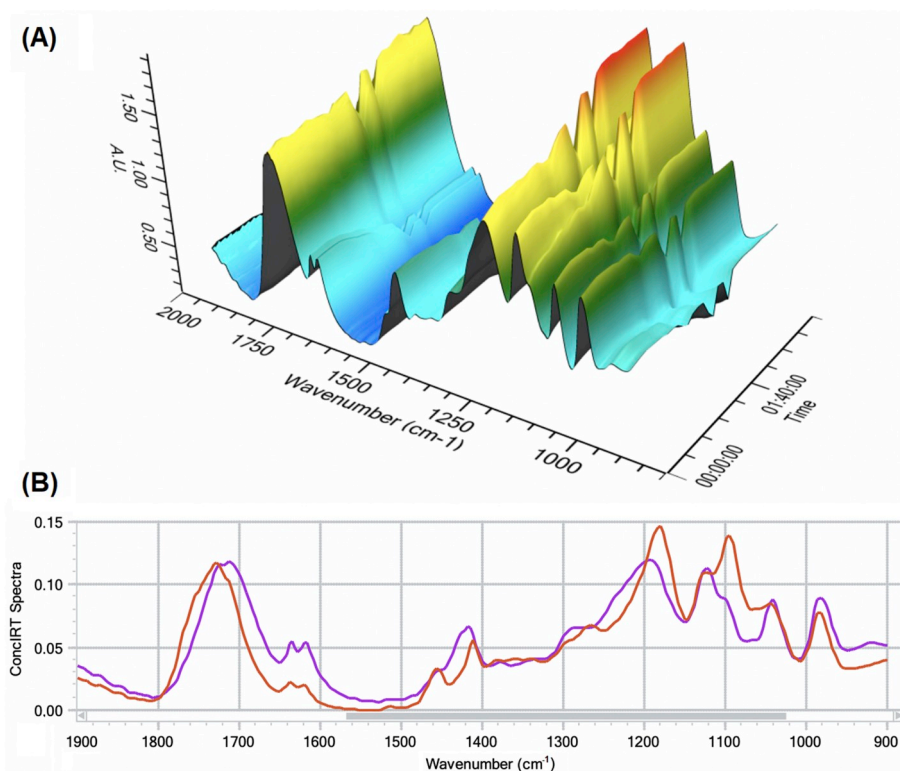


Fig. 2. Real time, in-situ FTIR measurements during lactic acid/acrylic acid batch esterification. (A) Spectral changes along batch reaction. (B) Deconvoluted spectra of the reactants (purple, related to the beginning of the reaction) and the product (red, associated to the end of the reaction). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

atactic and 60% syndiotactic configurations. This tacticity distribution reveals that polymer materials based on ELA and MMA are essentially amorphous, which converges with MMA-rich polymers (Allen and Williams, 1985; Lemieux and Prud'homme, 1998; Hsu and Mark, 1999).

According to Abe et al. (1968), the formation of MMA-based syndiotactic polymers takes place as a result of the preferred chain configuration in the free-radical polymerizations. As an additional information concerning the amorphous behavior of the synthesized polymers, Fig. S3 in the supplementary material shows typical XRD patterns of ELA/MMA copolymers, deconvoluted into gaussian distributions, exhibiting three characteristic peaks observed at $2\theta = 13.3$,

29.5 and 42.5°. The amorphous halos of polymers confirm their non-crystalline nature.

As illustrated in Table 1, ELA was significantly incorporated into the copolymer chains, exhibiting copolymer compositions that range from approximately 4 mol% to 15 mol%, which is very compelling since it indicates that the copolymerizations with higher amounts of ELA can be carried out.

The final polymer presented high yields with conversion in the range from 97% to 85%, leading to formation of very stable latexes with average particle size of the nanoparticles lying in the interval from 72 nm to 200 nm, as the ELA concentration was increased up to 20 wt%

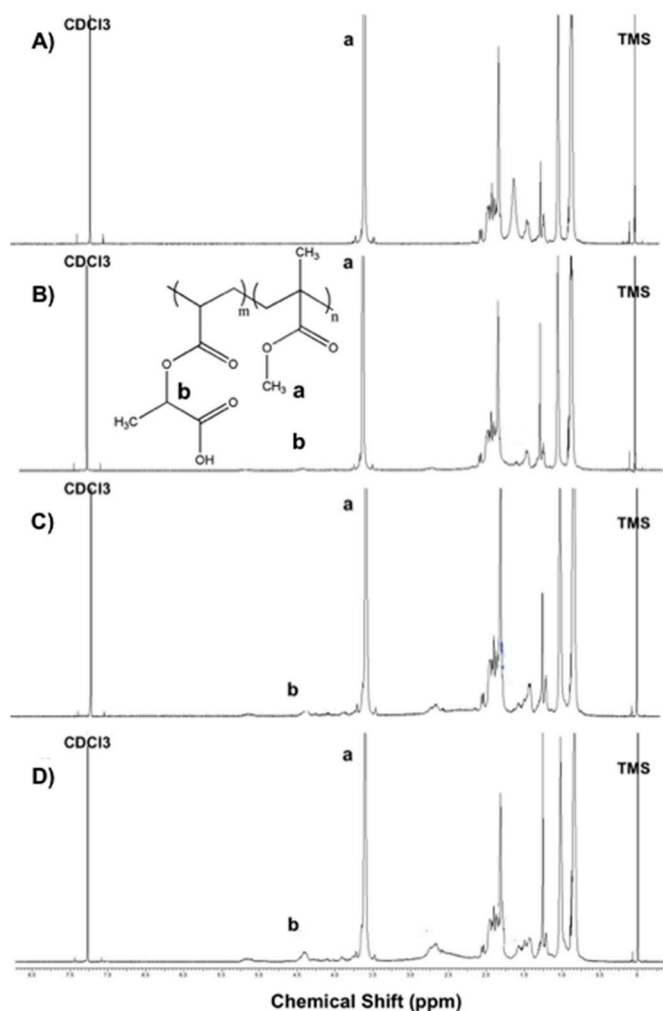


Fig. 3. ^1H NMR spectrum of (A) MMA homopolymer – Sample MMAELA00; (B–D) ELA/MMA Copolymers – Samples MMAELA05, MMAELA10 and MMAELA20, respectively.

(Table 1). The low polydispersity indexes [$\text{PDI} = \text{square of standard deviation}(\text{stddev})/\text{mean}, (\text{stddev}/\text{mean})^2$] indicate the formation of latexes of narrow particle size distribution in the polymer particles.

The average particle diameter (D_p) of the copolymer increases as the concentration of ELA is increased in the monomer nanodroplets. Considering that the emulsifier concentration was kept at the same value for all polymerizations, such an increase observed in the particle diameter is closely related to the high viscosity of ELA, thus becoming difficult to break up the monomer droplets during the sonication process. Consequently, the miniemulsion formed with higher amounts of the esterified lactic acid leads to the formation of bigger droplets.

According to both values of the average particle size and the conversion depicted in Table 1, it is reasonable to assume that a compartmentalized behavior takes place. For instance, samples MMAELA00 and MMAELA05 with D_p equal to 72.2 nm and 78.4 nm, respectively. In this

case, it is strongly expected the presence of single radicals into the polymer particles. Considering that each single radical may be confined in one polymer particle, the termination reaction rate between the radicals is significantly reduced, which leads to an increase in the reaction rates as the particle size is decreased. As a matter of fact, high reaction rates associated with polymer particles of small diameter are closely related to the zero-one kinetics occurrence, as the compartmentalization behavior is expected if the average number of radicals per particle is equal to or lower than one (Schork et al., 2005; Gilbert, 1995; Lovell and El-Aasser, 1997). Table 1 also shows that the reaction conversion varies with particle diameter, indicating a decrease in the reaction rate as the average particle size increases. This polymerization behavior reflects the compartmentalization effect of growing radicals inside the particles. Polymer particles exhibiting high volume contribute to the presence of more radicals inside the particles with high probability of termination (Costa et al., 2013).

The effect of the ELA concentration on the molar mass distribution (MMD) of the ELA/MMA copolymers is depicted in Fig. 4. It is observed that the incorporation of ELA plays an important role on the mass-average molar mass (M_w), leading to a significant reduction from approximately 10^3 kg mol^{-1} to 10^2 kg mol^{-1} as the ELA molar fraction increased up to 15 mol%. GPC measurements indicated that the lower the concentration of the modified lactic acid monomer in the copolymer, the higher the average molar masses. It is very important to notice that the shape of the MMD was also significantly changed from a narrow and unimodal to a broad and bimodal behavior, which means that the final properties of the MMA homopolymer are strongly changed by the incorporation of this esterified lactic acid.

The reduction in the mass-average molar mass (M_w) can be justified because the higher the monomer droplet is, the rate of initiator radicals entry into the polymer particles favors more effectively the termination rates between the growing polymer chains, which reduces the average molar masses (Jensen et al., 2016; Laurentino et al., 2018; Neves et al., 2018). As an effect of the compartmentalization of the radical of initiators, it is reasonable to expect that larger monomer droplets are more likely to present a higher average number of radicals per particle, resulting in lower average molar masses.

It is also worthwhile to observe the bimodal feature of the molar mass distribution of the copolymers that present approximately 9 mol% and 15 mol% of ELA with M_w of approximately 123 kg mol^{-1} and 98 kg mol^{-1} , respectively. According to Fig. 4, the shape of the MMD changes from narrow and unimodal (for MMA homopolymer) to broad and bimodal behavior (for ELA/MMA copolymers), suggesting that the final properties of the MMA homopolymer are strongly modified by the incorporation of ELA.

Another important aspect is that the miniemulsion compartmentalization plays an important role in the formation of polymer latexes with bimodal molar mass distribution (MMD) resulting from the limited volume effect (Fonseca et al., 2010; Tobita, 2003). As depicted in Fig. 4, narrow and unimodal MMDs (samples MMAELA00 and MMAELA05) are closely related to the polymer latexes of small size, whereas the broad and bimodal MMDs are associated to the polymer latexes presenting average particle size values higher than 100 nm (samples MMAELA10 and MMAELA20). The bimodality might be attributed to other factors, as for instance, the gel effect and the nature of the monomer reactivity ratios. In particular, when the role of the gel effect on the MMD is

Table 1

ELA/MMA-based polymers: average particle diameter (D_p), average molar masses (M_w and M_n), molar mass dispersity (D_M), glass transition temperature (T_g), copolymer composition (χ_{ELA}) and conversion.

Sample	ELA (g)	MMA (g)	D_p (nm)	PdI	M_w ($\text{g}\cdot\text{mol}^{-1}$)	M_n ($\text{g}\cdot\text{mol}^{-1}$)	D_M	T_g ($^{\circ}\text{C}$)	χ_{ELA} (%)	Conversion (%)
MMAELA00	0.0	6.0	72.2	0.060	1104591	451261	2.4	116	0.0	96.5
MMAELA05	0.3	5.7	78.4	0.169	294771	154174	1.8	105	4.3	96.0
MMAELA10	0.6	5.4	101.1	0.142	122526	11218	10.9	102	9.1	92.0
MMAELA20	1.2	4.8	201.5	0.221	98147	20593	4.8	86	15.1	85.0

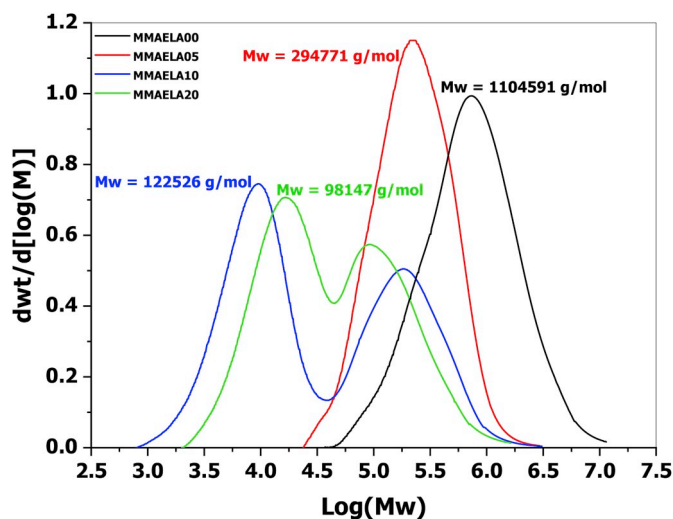


Fig. 4. Molar mass distributions of the ELA/MMA copolymers and the effect of increasing the concentration of ELA in the reaction system.

considered, it is reasonable to assume that broader MMDs may be obtained as a combined effect of the viscosity increase into the particles and a drastically decrease of the chain termination rates when the reaction conversion evolves, increasing the number of polymer particles that contain more than one radical (Costa et al., 2013). On the other hand, in our study, it is not plausible to assume that the monomer reactivity ratios strongly affect the molar mass distribution of the polymer particles, as the copolymer composition drift was not observed under the experimental conditions evaluated here.

As displayed in Table 1, the T_g of the polymeric materials decreases as the concentration of modified lactic acid increases, in comparison to MMA homopolymer, from 116 °C for the MMA homopolymer to 86 °C for the ELA/MMA copolymer containing approximately 15% of ELA. The comonomer composition seems to play a critical role on the T_g , enhancing the mobility of the copolymer chains when compared to that of the MMA homopolymer chains. These experimental results indicate that the T_g of MMA-based materials can be adjusted in situ, by controlled insertion of ELA molecules into the polymer chains during the polymerization reaction.

The thermal stability of the polymeric materials was evaluated through TGA and the thermogram curves are presented in Fig. 5. It is observed that polymeric materials undergo complete thermal

degradation at temperatures that range from approximately 200 °C–500 °C, characterized by presenting two significant weight losses: *i*) in the temperature range from 250 °C to 320 °C for the first weight loss, referred to the degradation of the unsaturated terminal groups, and *ii*), a strong weight loss observed in the narrow range between 320 °C and 450 °C, associated to the degradation of the saturated groups. Additionally, the weight loss at temperatures below 200 °C may be related to the water evolved and the decomposition of residual monomer and oligomers.

Additional ELA/MMA batch copolymerizations were carried out to evaluate the polymerization behavior, providing the profiles of polymer particles diameter, average molar masses, T_g and copolymer composition along with each reaction time, as shown in Table 2 (N. B. experimental results correspond to individual batch reactions). Very stable polymeric latexes were synthesized with average particles size in the range from 72 nm to 79 nm. The very small scattering of D_p values is closely associated with unavoidable batch-to-batch variations and should be neglected.

According to Table 2, ELA/MMA copolymers with relatively high mass-average molar mass were synthesized ($230 \text{ kg mol}^{-1} < M_w < 426 \text{ kg mol}^{-1}$) with T_g increasing from approximately 95 °C–102 °C along the polymerization. The observed reduction in T_g values in comparison to MMA homopolymer ($T_g = 116$ °C) reflects the amount of ELA incorporated into the copolymer chains, maintained almost constant around 7 mol% throughout the polymerization process. It is also interesting to observe that the fraction of ELA incorporated into the copolymer chains decreases slightly throughout reactions, which characterizes the absence of an undesirable copolymer composition drift. Therefore, it is indicated that materials with homogeneous compositions can be easily synthesized without numerical controlling strategies, normally associated with the manipulation of the monomer feed flow rate based on a stochastic optimization procedure (Machado,

Table 2

ELA/MMA copolymer data: average particle diameter (D_p), mass-average molar mass (M_w), molar mass dispersity (D_M), glass transition temperature (T_g) and copolymer composition (χ_{ELA}).

Time (min)	D_p (nm)	PdI	M_w (g/mol)	D_M	T_g (°C)	χ_{ELA}
20	72.5	0.092	230119	2.50	95	8.2
40	71.5	0.082	308178	2.70	96	7.2
60	72.4	0.090	263795	2.26	100	6.3
90	72.2	0.100	280158	2.44	98	7.2
120	73.6	0.103	339689	2.54	102	7.2
180	79.2	0.122	426196	3.17	101	7.2

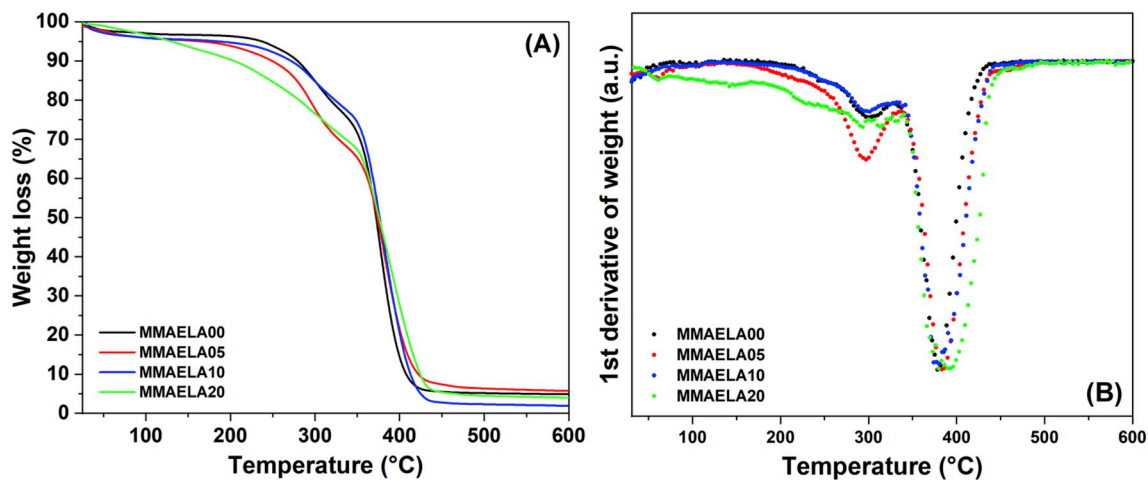


Fig. 5. Thermogravimetric analysis of the polymeric materials. (A) Weight loss of the polymer materials based on ELA and MMA monomers; (B) First derivative of weight of the polymer materials based on ELA and MMA monomers.

2019).

4. Conclusions

In conclusion, this work demonstrated that materials obtained from the modification of lactic acid have the potential to be used as monomers in free-radical polymerizations aiming at the production of new polymeric materials by employing an aqueous dispersion miniemulsion process to produce valuable environmentally friendly polymer materials.

It was also demonstrated that the modified lactic acid (ELA) can be employed in combination with classical vinylic monomers such as methyl methacrylate to synthesize copolymers with different compositions, presenting high reaction conversions with very stable polymer latexes. Considering the macromolecular properties of MMA homopolymer, it was observed that the T_g was significantly reduced as a result of the incorporation of ELA into the copolymer chains, particularly for the average molar masses. Moreover, it was demonstrated that the M_w and M_n were also significantly reduced as the molar fraction of ELA increased and, additionally, ELA/MMA copolymers exhibiting well-defined bimodal molar mass distribution were formed when the ELA molar fraction was higher than 9 mol%.

In short, the novel approach elaborated in this work allowed for the synthesis of new class of lactic acid-based materials by employing aqueous dispersion process to produce valuable environmentally friendly polymer materials.

Author contributions

All authors have contributed to the writing of the manuscript and they all have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scp.2019.100211>.

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