Bulk Polytransesterification of L-Lactic Acid Esters: An Alternative Route to Synthesize Poly(lactic acid)

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ABSTRACT: The synthesis of poly(lactic acid) (PLA) by bulk polytransesterification of different L-lactic acid esters was successfully carried out. The experiments were performed in two steps: a first one at 170°C, maximum temperature, and atmospheric pressure, to obtain a viscous oligomer; and a final step at 180°C and under reduced pressure to improve the byproduct elimination and increase the polymerization degree. The ethyl L-lactate polytransesterification in the presence of the binary catalytic system $Sb_2O/Zn(O_2CCH_3)_2 \cdot 2H_2O$ allowed achieving the highest average molecular weight, 22,300 g mol^{-1}. The yellowing of the melt polymer samples was recorded. The resulting materials were subjected to several characterization techniques: the chemical structure of PLA was confirmed by ^{1}H-NMR, the molecular weight was determined by size exclusion chromatography, thermal behavior measured by differential scanning calorimetry and racemization extent by specific rotation measurements. A special attention was paid to the polymer optical purity, as it is of major importance to assess its quality and the significance of the synthesis route. To the best of our knowledge, there is no previous report dealing with the synthesis of PLA by bulk polytransesterification. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: biodegradable; polyesters; renewable resources; polytransesterification; poly(lactic acid)

INTRODUCTION

Since the early studies carried out by Carothers, polyesters have become one of the most versatile classes of polymers. Among them, poly(ethylene terephthalate) (PET), widely used to manufacture fibers and bottles,[1,2] is the most important one. In the last decades, the need to develop sustainable alternatives to petrochemical origin materials associated with an increasing demand for biodegradability[3,4] has led to a remarkable interest in aliphatic polyesters such as poly(lactic acid) (PLA). Thus, the development and improvement of synthesis processes involving environmental friendly materials is extremely important in enabling its future implementation by the industry and therefore in expanding the use of these materials.

PLA is a thermoplastic polyester obtained from renewable raw materials with the ability to undergo hydrolytic and biological degradation. These features make it very attractive for bioresorbable and environmentally degradable materials,[3–5] with a foreseeable wide range of applications from biomedical and pharmaceutical goods to the conventional large scale utilization polymers such as fibers, films, and packaging.

The synthesis of PLA by conventional polycondensation was originally studied by Carothers. However, the resulting material exhibited low-molecular weight and poor mechanical properties,[6] unsuitable for commercial applications. Currently, commercially available PLA is synthesized by a multistep process called ring opening polymerization (ROP) of lactide, an intermediate compound.[3,4] It is an effective but quite complex process justifying the effort to develop a more efficient and inexpensive route.

Several research groups[7–12] have been studying the synthesis of PLA by conventional step-growth polymerization methods, commonly used for large-scale production of commercial polyesters. Moon and Kimura[7] studied the direct lactic acid bulk polycondensation, but high-molecular weight PLA could not be achieved due to inefficient water removal during the polymerization. Similar findings were recently published by Sedlarik et al.,[9] where the highest molecular weight achieved by lactic acid bulk polycondensation was 17,200 g mol^{-1}. Chen et al.[10] were able to obtain PLA with 130,000 g mol^{-1} by direct lactic bulk polycondensation by increasing the reaction time up to 40 h. However, a negative impact on polydispersity index (PD) was registered and the yellowing phenomena observed in bulk polymerizations were not properly assessed.

Ajioka et al.[11] studied the lactic acid polycondensation in solution, using organic solvents to reduce the viscosity of the reaction medium and enabling continuous water removal. They obtained molecular weights higher than 100,000 g mol^{-1}, thus confirming water removal as a key factor to increase reaction extent and molecular weight. A previous work[12] reported the synthesis of high-molecular weight PLA, up to 80,000 g mol^{-1}, in xylene. Although the molecular weight was high, resorting to organic solvents narrows the range of PLA applications and does not contribute to a sustainable environment, therefore supporting the search for alternative routes.

While the lactic acid polycondensation has been recently studied, the polytransesterification of lactic acid esters has not been tested yet. To the best of our knowledge, there is no previous record on the use of lactic acid esters as monomers for the PLA synthesis by polytransesterification. On the other hand, the procedure for purification of lactic acid obtained by fermentation[13,14] usually requires an esterification step, and a subsequent hydrolysis of the ester to revert it to lactic acid. The use of these esters for PLA synthesis would enable simplifying the lactic acid purification process while avoiding the synthesis and purification of the lactide. Therefore, it would offer intelligible advantages over ROP and over lactic acid polycondensation. Moreover, the end group protection in the polylactide has been reported as an additional factor toward thermal stability,[15] increasing the degradation temperature by 10°C.

Preliminary experiments involving the polytransesterification of different L-lactic acid esters were successfully carried out. Figure 1 shows the simplified polytransesterification mechanism of the different L-lactic acid esters tested in this experimental work. The polymerization main product is PLA with carboxylic end group protection and the byproduct is an alcohol, whose chemical structure depends on the monomer used.

EXPERIMENTAL

Materials

All reagents were ordered from Sigma-Aldrich and used as received. Ethyl L-lactate 98%, methyl L-lactate 97%, isopropyl L-lactate 97%, and butyl L-lactate 97% were used as monomers. The catalysts tested were: tin (II) chloride dihydrate 98% (SnCl$_2$·2H$_2$O), tin (II) octoate 98% (SnOct), antimony (III) oxide 99% (Sb$_2$O$_3$), zinc acetate dihydrate 98% [Zn(acet)], manganese (II) acetate tetrahydrate 99% [Mn(acet)], tin powder 99.8% (Sn), and titanuim (IV) butoxide 97% (TNBT). The solvents, HPLC grade chloroform, chlo-
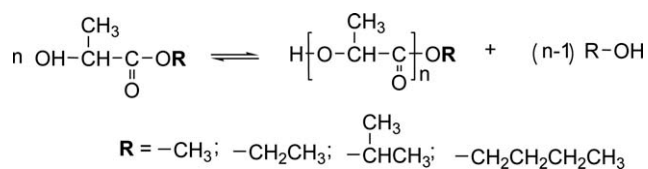

Figure 1 Polytransesterification mechanism of different L-lactic acid esters.

roform and ethanol, were purchased from Panreac and used without further purification.

Bulk polytransesterification of L-lactic acid esters

The experiments were carried out in a 500-mL glass vessel equipped with a heating mantle, a mechanical stirrer, temperature and pressure sensors, and a partial condenser connected to a vacuum system through a cold trap.[16] During the experiment, the temperature and pressure are controlled by a PLC and registered. The initial amount of L-lactic acid ester (200 mL) and catalyst or catalytic system were introduced in the reaction vessel and allowed to react overnight under inert atmosphere at 100 rpm. The heating up process takes ∼ 4 h until reaching the temperature set-point—170°C. Then, the temperature set point was increased to 180°C and a time span of 1 h was allowed before starting the gradual pressure reduction from atmospheric to 10 mbar (set-point) carried out for 4 h. Finally, after reaching the pressure set-point, the reaction proceeded under these conditions, $T = 180$°C and $P = 10$ mbar, for another 3 h. The final polymer, in the form of a brown or light brown viscous melt, was allowed to cool to room temperature and recovered as powder after dissolution in chloroform and precipitation in fourfold ethanol.

Characterization techniques

Size exclusion chromatography measurements

The average molecular weight (M_w), number molecular weight (M_n), and PD were determined by size exclusion chromatography (SEC). The chromatograph was calibrated with narrow polystyrene standards (4000, 10,050, 19,880, 30,300, 66,350, 96,000, and 200,000 g mol^{-1}). The column set consists of a Polymer Laboratory 5-μm guard column (50 × 7.5 mm^2) followed by one PL gel 5-μm MIXED-D column (300 × 7.5 mm^2). The HPLC pump was set with a flow rate of 0.6 mL min^{-1} and the eluent was HPLC grade chloroform. After purification by precipitation, ∼ 2 mg mL^{-1} polymer sample was prepared and the SEC measurements were carried out at 25°C. Before the injection (∼ 50 μL), the samples were filtered through a PTFE membrane with 0.45 μm pores. After column exclusion, the samples were

TABLE I
Results Obtained in Different L-Lactic Acid Esters Bulk Polytransesterification Experiments Using a Two-Step Process
(T_1 = 170°C and P_1 = 1 bar; T_2 = 180°C and 10 mbar $\langle P_2 \rangle$ 1 bar)

PLA	Lactate	Catalyst (% w/w)[a]	Co-catalyst (1% w/w)	M_w (g mol^{-1})	PD	T_g (°C)	T_m[b] (°C)	X_c (%)	OP (%)	Appearance
PLA1	Ethyl	Sb$_2$O$_3$ [0.25]	–	12,700	1.7	53	154	43	86	White
PLA2	Ethyl	Sb$_2$O$_3$ [0.5]	–	15,300	1.3	50	152	37	85	Pale yellow
PLA3	Ethyl	Sb$_2$O$_3$ [1]	–	14,300	1.4	50	152	37	85	Pale yellow
PLA4	Ethyl	Sb$_2$O$_3$ [0.25]	Zn(acet)	22,300	1.4	54	155	47	85	White
PLA5	Ethyl	Sb$_2$O$_3$ [0.25]	Mn(acet)	11,300	1.5	48	147	34	82	White
PLA6	Ethyl	Sn(Oct) [0.25]	Zn(acet)	17,800	1.4	55	143	14	78	Pale yellow
PLA7	Ethyl	SnCl$_2$ [0.25]	Zn(acet)	20,700	1.3	55	nd	0	65	Pale yellow
PLA8	Ethyl	TNBT [0.25]	Zn(acet)	5000	1.4	47	145	41	88	White
PLA9	Ethyl	Sn [0.25]	Zn(acet)	6500	1.8	49	144	48	83	White
PLA10	Methyl	Sb$_2$O$_3$ [0.25]	Zn(acet)	9400	1.4	44	nd	0	67	Pale yellow
PLA11	iPropyl	Sb$_2$O$_3$ [0.25]	Zn(acet)	8500	1.4	48	nd	0	68	Pale yellow
PLA12	Butyl	Sb$_2$O$_3$ [0.25]	Zn(acet)	17,200	1.6	52	144	41	87	White

[a] Weight ratio (catalyst/initial monomer).
[b] Taken from the first heating scan.
nd, Not detected.

analyzed in an evaporative light scattering detector, PL-EMD 960. Data processing was carried out with GPC Clarity software from DataApex.

NMR measurements

The ^{1}H-NMR spectra of PLA were recorded on a Varian 500-MHz spectrometer at 25°C using deuterated chloroform, CDCl$_3$, as solvent containing 1% (v/v) of tetramethylsilane as internal standard.

Specific rotation measurements

The specific rotation of PLA polymers, $[\alpha]_\lambda^T$, was measured with a optical activity AA-5 electrical polarimeter at 25°C, with a wavelength of 589 nm and a concentration of 1 g dL^{-1} in chloroform. The percentage of optical purity (OP) of PLA polymers was calculated using the following relationship[12]:

$$OP(\%) = \frac{[\alpha]_{589}^{25}}{-156} \times 100 \qquad (1)$$

where −156 is the specific rotation of PLA with only L-stereoisomer in its composition.[12]

Differential scanning calorimetry measurements

Glass transition temperature (T_g), melting point (T_m), and fusion enthalpy (ΔH_m) were measured using a differential scanning calorimetry (DSC) equipment, SDT Q600 from TA Instruments, under nitrogen atmosphere, with a heating rate of 10°C min^{-1}. The samples were analyzed in two heating scans in the range 30–200°C. The percentage of crystallinity (X_c) was calculated using the following relationship[17]:

$$X_c(\%) = \frac{\Delta H_m}{93} \times 100 \qquad (2)$$

where 93 J g^{-1} is the fusion enthalpy of a PLA crystal of infinite size.[17] Universal analysis 2000 software from TA Instruments was used for data processing.

RESULTS AND DISCUSSION

The experimental work reported here was mainly focused on assessing the experimental conditions required to synthesize PLA by bulk polytransesterification of different commercially available L-lactic acid esters. The experimental conditions: monomers, catalysts or catalytic systems, and catalyst concentration; as well as the results achieved: molecular weight, thermal properties, OP, and visual appearance are compiled in Table I.

Bulk polytransesterification of ethyl L-lactate

The first stage of this work was carried out using ethyl L-lactate as monomer for the polytransesterification process (PLA1–PLA9). Preliminary experiments, not shown here, revealed that in the absence of a metal-based catalyst, the entire monomer was withdrawn during the initial stage of the process, which was carried out at atmospheric pressure and no polytransesterification took place. This finding is contrary to previous lactic acid polycondensation results,[12] where it was reported that the monomer polymerizes in the absence of an external catalyst.

After this preliminary assessment, the experimental procedure was altered and carried out in two different steps. A first step in the presence of a metal-
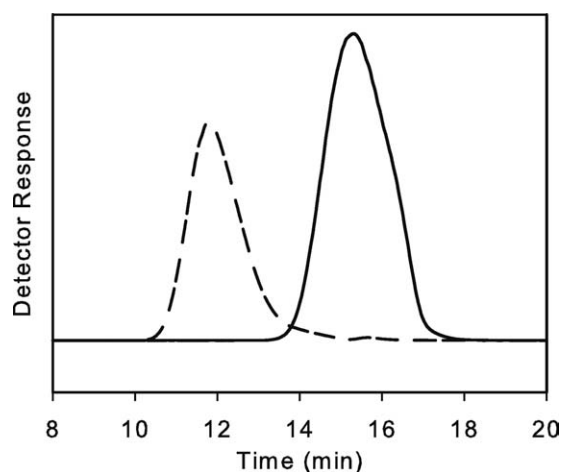
Figure 2 Typical molecular weight distribution obtained by SEC for polytransesterification products: oligomers after the first step (—) and final polymer (–).

based catalyst, at temperature set-point of $170°C$ and atmospheric pressure, allowed monomer transesterification and led to a viscous oligomer. The final step was carried out at $180°C$ and reduced pressure, to shift the reaction toward polymer production by means of a more efficient byproduct elimination. During the polytransesterification process, the partial condenser has an important role to selectively distil off the alcohol byproduct and reflux the monomer, avoiding its elimination. At the end of the experiments, close to 100 g of polymer and 100 mL of distillate, alcohol, and monomer were collected. The final product was investigated by molecular weight distribution measurements, thermal properties, OP, and visual appearance after polymer precipitation from chloroform solutions. The color of the final materials ranged from white to a pale yellow powder, depending on experimental conditions. In trading, the polyesters color is an important quality parameter, and therefore it is used here for qualitative assessment. The typical molecular weight distributions of the oligomers and final polymer, obtained by SEC, are presented in Figure 2 confirming the expected increase in molecular weight in the second step of the polytransesterification.

Catalyst screening

Polytransesterification, as explained above, is a slow reaction requiring the addition of a metal-based catalyst. There is no information available in the literature regarding the chemical synthesis of PLA by polytransesterification. The information on the best catalysts to be screened was gathered from PET polytransesterification process and from previous results on PLA synthesis by polycondensation.[1–8] Table I summarizes the catalysts/catalytic systems studied and the results obtained (PLA1–PLA9),

while studying the ethyl L-lactate polytransesterification. In Table I, it is noticeable that the catalyst employed has a dramatic influence on the final polymer properties.

The work reported in this manuscript began by studying three different contents of antimony III oxide (Sb_2O_3) (PLA1–PLA3) a Lewis acid widely used in the PET synthesis by dimethyl terephthalate polytransesterification with ethylene glycol.[1,2] As shown in Table I, the catalyst concentration plays an important role in the final molecular weight and color change. Slightly higher molecular weights were obtained when using a catalyst content of 0.5 and 1% w/w (weight of catalyst/initial weight of monomer). However, color change suggests the occurrence of thermo-oxidative degradation reactions. Based on these results, 0.25% w/w of Sb_2O_3 was selected as the optimal catalyst content for further experiments. The addition of 1% w/w of zinc acetate as a co-catalyst of Sb_2O_3 (PLA4) allowed a considerable increase in the molecular weight, from 12,700 to 22,300 g mol^{-1}, the best result in Table I both in terms of molecular weight and polymer color. Testing zinc acetate as sole catalyst, experiment not shown in Table I, did not lead to a polymer. Although the mechanism has not been fully understood, the addition of zinc acetate as a co-catalyst of Sb_2O_3 had a synergic effect. Manganese acetate was also tested as a co-catalyst (PLA5), but the molecular weight was lower than obtained before when using only Sb_2O_3. Several other compounds reported in the literature as efficient polyesterification or polytransesterification catalysts were tested making use of the binary catalytic system approach (PLA6–PLA9). Among the catalytic systems examined, the Sb_2O_3/Zn acetate was confirmed as the most effective, enabling better polymer properties. The molecular weight of PLA7 was also greater than 20,000 g mol^{-1}, ranking high the performance of $SnCl_2·2H_2O$ as a polytransesterification catalyst, but the yellowing of the final polymer and the low OP measured discourages its further utilization. $SnCl_2·2H_2O$ is a strong Lewis acid largely used in bulk polycondensation of lactic acid.[7] Therefore, the 68% OP of PLA7, the lowest among the entire series of polymer samples, was an unexpected result. The addition of TNBT (PLA8) led to poor results in terms of molecular weight, but it was the most efficient catalyst in terms of polymer stereoregularity control, exhibiting the highest OP degree, 88%. The OP issue and its influence on polymer properties will be discussed in a further section of this work. The PD of all samples was below 2, fulfilling requirements for commercial applications.

Influence of different monomers

Aiming at studying the influence of the alkyl substitute group on the polytransesterification reaction,

other L-lactic acid esters such as methyl, isopropyl, and butyl L-lactate have been tested. The same experimental conditions (time, temperature, and pressure) and the catalytic system selected from the ethyl L-lactate experiments (0.25% w/w of Sb_2O_3 and 1% w/w of Zn acetate) were implemented, and the samples obtained are listed as PLA10, PLA11, and PLA12 (Table I).

As it would be expected, the length of the alkyl substitute group in the different L-lactic acid esters has a great influence on the polymerization performance. Polytransesterification is an equilibrium reaction reported in the literature[1] as an $A_{AC}2$ addition-elimination mechanism that proceeds through a substitution reaction at the carboxyl carbon, with the formation of a tetrahedral intermediate, followed by the elimination of the leaving group, i.e., the alkyl substitute group. According to Rogers and Long,[1] nucleophilic attack on the carbonyl group by the alcohol is a key step in the substitution process being strongly dependent on the nature of the leaving group. The steric effect of bulky groups close to the reaction site does not favor the ester formation, which might explain the poor result obtained while using isopropyl L-lactate (PLA11). However, the steric hindrance effects do not explain the poor results obtained when using methyl L-lactate (PLA10).

Among the L-lactic acid esters tested, methyl L-lactate has the lowest boiling point, 144°C. Differently from other records, at the end of experiment 10, a larger volume of distillate, 140 mL, and a smaller weight of polymer, 50 g, were collected. This vaporization of methyl L-lactate has certainly changed the monomer/catalyst ratio during the process and this may explain the poor properties of PLA10.

According to the experimental results in Table I, ethyl L-lactate allowed achieving the best product and might be the best choice for PLA synthesis by polytransesterification. This finding is contrary to PET synthesis process, where dimethyl terephthalate is the monomer usually employed.[2]

Thermal characterization

Information on the thermal behavior of materials is relevant to evaluate the physical properties and processing conditions of semicrystalline polymers. Therefore, the polymer samples obtained in the frame of this work were subject to DSC analysis. The glass transition temperature (T_g), the melting point (T_m), and the crystallization degree (X_c), evaluated from fusion enthalpy of the first heating scan, are also summarized in Table I. Figure 3 shows the DSC traces of the samples obtained in the second heating scan.
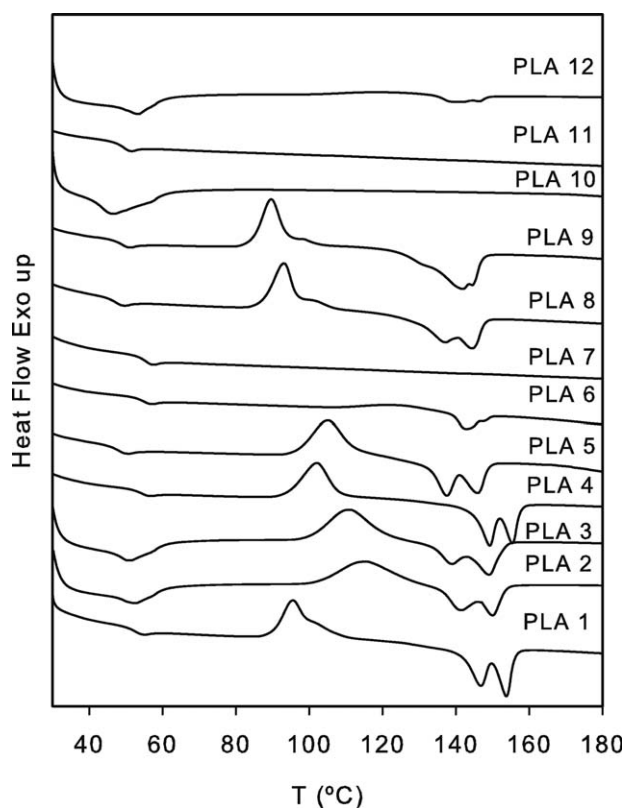

Figure 3 DSC traces from second heating scan of the PLA samples.

It is easily noticed in Figure 3 that the thermal properties of the samples are greatly different and the polymers range from semicrystalline (PLA1-6, PLA8, PLA9, and PLA12) to amorphous behavior (PLA7, PLA10, and PLA11). As expected, glass transition and melting temperature are highly dependent on molecular weight and the data registered in Table I are generally in agreement with this trend. As the molecular weight increases, the molecular mobility becomes restricted influencing its thermal behavior. In Table I, the glass transition temperature (T_g) ranges from 44 to 55°C and the PLA's melting temperature (T_m) from 143 to 155°C. Both temperature ranges are lower than those reported for commercial polylactides[3] but are in agreement with previous results for PLA in the same molecular weight range,[7–9] although produced by lactic acid polycondensation. Moreover, as shown in Figure 4, the experimental glass transition temperature, full symbols, is in good agreement with the theoretical values [Eq. (3)], empty symbols. Despite the clear trend (Fig. 4) of increasing T_g with molecular weight, the experimental values are slightly scattered, which can be due to discrepancies in the OP degree. The introduction of D-lactyl unities in the main polymer chain alters the chain mobility and has a strong impact on thermal properties. The T_g theoretical values were obtained with Fox–Flory equation[18]:
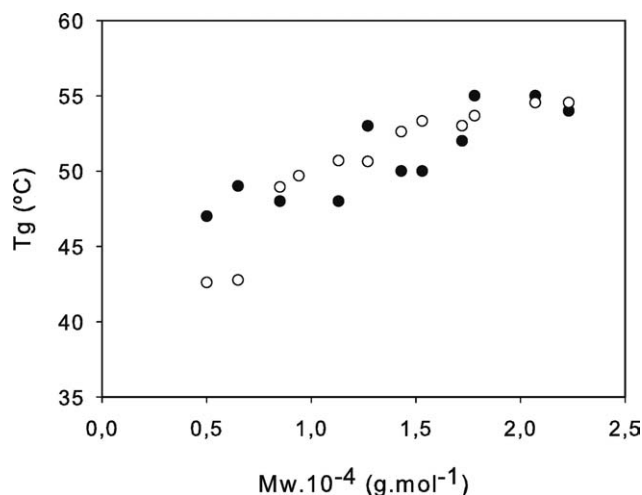
Figure 4 PLA sample's glass transition temperature versus molecular weight: (●) experimental obtained by DSC and (○) theoretical, obtained with Fox–Flory equation [Eq. (3)].

$$T_g(^\circ C) = T_g^\infty - \frac{K}{M_n} \qquad (3)$$

where, according to Jamshidi et al.,[18] the glass transition temperature of PLLA with a infinite molecular weight, T_g^∞, is 58°C, and K is 5.5×10^4, a constant representing the influence of the excess free volume of the polymer end groups. It is worth mentioning that Eq. (3) fails in the low-molecular weight region. This can be attributed to the influence of the carboxylic end group protection, which might have a stronger influence on the low-molecular weight polymer chains. Additionally, the Fox–Flory parameters reported by Jamishidi et al.[18] were recorded with polylactides with free end groups and not protected ones, as those produced in this experimental work.

The Flory equation can also be used for predicting the melting point as function of the molecular weight and Jamshidi et al.[18] reported the Flory equation parameters for this purpose. This equation fits well for polymers with high-molecular weight but not in the low range,[3,18] therefore this comparison was not addressed here.

Regarding the data in Table I, it is important to refer that the crystallinity degree showed to be highly dependent on the catalyst and monomer used during the polymerization and ranged from 0 to 48%. The catalysts that allowed reaching the highest crystallinity degree were tin powder and Sb_2O_3, 48% and 47%, respectively. On the other hand, $SnCl_2 \cdot 2H_2O$ produced the worst result, 0%, as the DSC trace of PLA7 (Fig. 3) does not exhibit the peak corresponding to the melting. Similar findings were reached with polymers synthesized from methyl and isopropyl L-lactate (PLA10 and PLA11) suggesting an amorphous structure.

Several factors affect the crystallization process of PLA such as molecular weight, thermal history, and L/D-lactyl isomers ratio. The occurrence of two melting peaks in the second heating scan of PLA samples (Fig. 3) is a consequence of its complex crystallization behavior. According to Wang and Mano,[19] several mechanisms have been proposed to explain the origin of this phenomenon; however, this is still under discussion. Nevertheless, it is usually accepted that the presence of different crystalline structures and the simultaneity and competitiveness of the melting and recrystallization processes leads to this result.

Racemization

The yellowing of the final polymer suggests the occurrence of undesirable degradation reactions during the bulk polytransesterification, and this is further supported by the OP results. The occurrence of racemization reactions, also identified in ROP and polycondensation mechanisms, are responsible for introducing some D-lactyl units in the polymer chain and, consequently, for affecting the polymer stereoregularity. The origin of this kind of reactions was reported earlier[7,8,12,20] and, therefore, will not be discussed here.

It is well known that PLA stereoregularity strongly influences its crystallinity and thermal behavior, which can explain some disagreement between molecular weight and thermal characterization discussed above. To clarify this issue, the influence of OP on crystallization degree is addressed in Figure 5. It is clear that the crystallinity decreases sharply with the decrease in the OP, and for OP lower than ∼ 70%, the polymers are amorphous. This finding is similar to the results reported earlier by Tsuji and Ykada.[21] This cumulative information
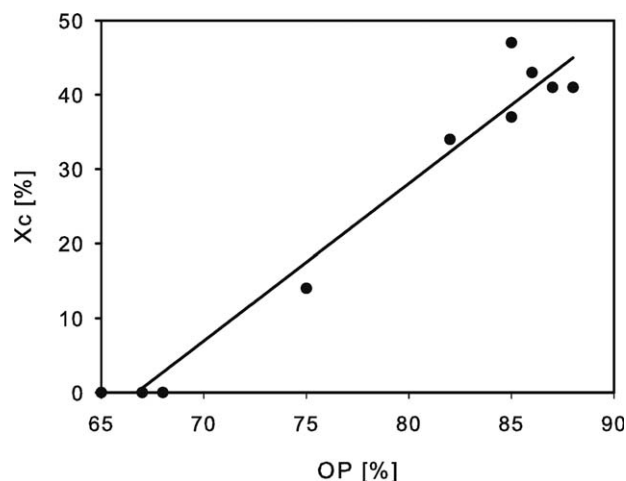

Figure 5 Crystallinity degree versus OP of the PLA samples.

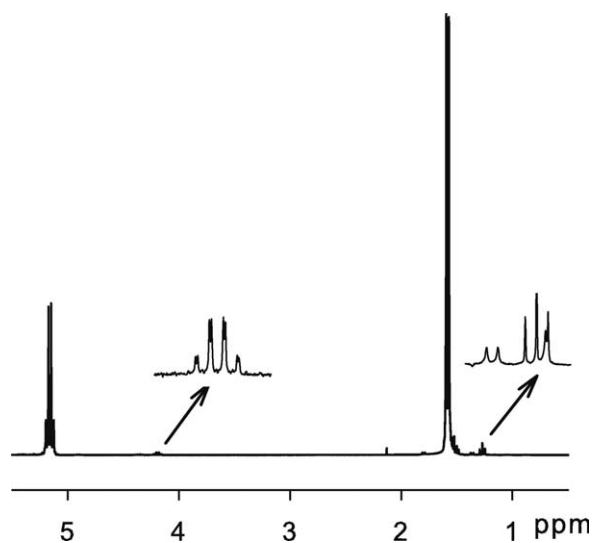**Figure 6** ^{1}H-NMR spectrum of PLA4.

renders perceptible that the D-lactyl units, introduced due to racemization reactions, hindered the crystallization process.

NMR spectroscopy

The typical chemical structure of PLA was confirmed in the ^{1}H-NMR of the samples. Figure 6 shows the ^{1}H-NMR of PLA4 (M_w = 22,300 g mol^{-1}) corroborating the successful polytransesterification of the ethyl L-lactate. The large quartet and doublet at 5.15 and 1.57 ppm are assigned to the methine, —CH(CH$_3$)—OCO—, and methyl, —CH(CH_3) —OCO—, protons in the main chain. The weak quartet at 4.208 ppm is assigned to the methine in the chain end units and the series of weak peaks downfield, 1.25 and 1.35 ppm, are assigned to the ethyl end groups.

CONCLUSION

PLA was successfully produced by direct bulk polytransesterification. Several L-lactic acid esters were tested and the results revealed that their structure influences the final molecular weight (*i*propyl < methyl < butyl < ethyl). The activity of the catalysts screened disclosed differences and pointed to the utilization of Sb$_2$O$_3$ for best results (TNBT < Sn < Sn(Oct) < SnCl$_2$ < Sb$_2$O$_3$). The addition of Zn(O$_2$CCH$_3$)$_2$·2H$_2$O to Sb$_2$O$_3$ showed a synergic effect, which enabled synthesizing the PLA sample with the highest molecular weight, 22,300 g mol^{-1}. This binary catalytic system was also effective for suppressing racemization allowing a colorless polymer.

The thermal behavior of the materials obtained is strongly dependent on final molecular weight and OP. Under certain experimental conditions, the catalysts tested also promoted racemization reactions during polymerization, leading to a decrease in polymer crystallinity. The catalyst influence upon racemization extent was found to be (SnCl$_2$ > Sn(Oct) > Sn > Sb$_2$O$_3$ > TNBT). Specific rotation measurement confirmed to be a powerful technique to evaluate the racemization extent and the stereoisomer composition of the lactyl units in the polymer chain. Lactic acid polymers with an OP below 70% showed an amorphous structure.

From the economic point of view, it is of best interest to develop an efficient, effective, and less expensive route to produce PLA. These results support that the polytransesterification can be envisaged as a promising alternative for PLA synthesis. However, further research work needs to be carried out to find the best reaction conditions enhancing the molecular weight and avoiding undesired side reactions.

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