Improving Lactic Acid Melt Polycondensation: The Role of Co-Catalyst

Dina S. Marques, Maria H. Gil, Cristina M. S. G. Baptista

Department of Chemical Engineering, Faculty of Sciences and Technology University of Coimbra, Polo II, Coimbra 3030-790, Portugal
Correspondence to: D. S. Marques (E-mail: dinam@eq.uc.pt)

ABSTRACT: A study on lactic acid polycondensation under melt conditions was carried out and a preliminary assessment revealed tin powder as a very good catalyst for poly(lactic acid) (PLA) synthesis by melt polycondensation while confirming previous information on $SnCl_2$ good performance. However, these catalysts also promoted side reactions leading to racemization and yellowing of the final polymer. The use of p-toluenesulphonic acid (p-TSA) or triphenylphosphine (PPh_3) as co-catalysts proved to be very effective hindering colour formation and allowing synthesizing PLA samples with enhanced properties. The addition of these compounds to neat tin powder increased the PLA optical purity, whereas their addition to $SnCl_2$ speeded up the polymerization. A significant increase in molecular weight, from 32,500 to 52,000 g mol^{-1}, was recorded, with the new catalytic system $SnCl_2/PPh_3$ showing catalytic activity comparable with the one reported in the literature for $SnCl_2/p$-TSA. Several characterization techniques were used for assessing polymer samples: the molecular weights were determined by SEC, thermal behavior measured by DSC, and racemization extent calculated from specific rotation measurements. UV/vis spectroscopy was confirmed as a powerful technique for evaluating yellowing of final polymers. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly(lactic acid) (PLA) is a synthetic biodegradable material obtained from a 100% renewable monomer, the lactic acid, being one of the most promising substitutes for petrochemical origin materials. The chemical, mechanical, and physical properties of the PLA allow a wide range of applications from biomedical to conventional large-scale polymer uses. In addition, this biodegradable polymer can be easily processed employing thermoplastics' conventional techniques such as injection molding, thermoforming, and extrusion. In recent years, these characteristics have led to a growing PLA economical relevance[1–3] and prospects of an increasing commercial interest are foreseen for the near future. These are compelling driving forces for the development of new synthesis routes and the upgrading of current production processes for this environmentally friendly material.

The industrial large-scale production of high-molecular weight PLA involves the ring opening polymerization (ROP) of an intermediate compound, the lactide, in the presence of stannous octoate catalyst.[1–3] This is an effective but quite complex process involving high energy consuming stages, increasing the production costs and the process environmental footprint, therefore supporting the effort to develop an alternative route.

The large-scale production of commercial polyesters such as poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT)[4,5] has encouraged several research groups[6–15] to study the synthesis of PLA by direct melt polycondensation. However, the synthesis of high quality PLA under melt polycondensation conditions, which entangle temperature above melting point and long reaction times, remains a challenge. Under such operating conditions changes in the chemical structure of the growing polymer chain are introduced[1,2] and these may alter polymer properties. The most jeopardizing consequences are reduced optical purity (OP), due to racemization, and yellowing, a result of thermo-oxidation reactions. A decrease in OP has an adverse effect upon the thermal and mechanical properties and discoloration becomes a critical issue when applications require optically clear materials. According to Scheirs and Long,[4] the degradation products may even influence polymer organoleptic properties, as for example acetaldehyde present during PET production.

One of the most interesting studies on the direct melt polycondensation of lactic acid was carried out by Chen et al., in 2006, obtaining high-molecular weight PLA, 130,000 g mol^{-1}, by increasing the reaction time up to 40 h. Nevertheless, a negative impact on polydispersity (PD) index and on the (OP) was reported, besides the yellowing phenomenon observed during

the melt polymerization, which was not properly discussed. Moreover, the reaction time required by their process is excessive from an industrial point of view. Moon et al. was the first research group to discuss melt polymerization for PLA synthesis and to report that the addition of some compounds, such as proton acids, to a tin-based catalyst during polymerization could have a beneficial effect on the melt polymer thermal stability,[7,8] as well as on the polymerization rate. Based on these results a sequential process of melt polycondensation followed by solid state polycondensation was successfully developed[9,10] similar to the PET process.

Aiming at developing an alternative process for production of high quality PLA, this work details a study on the experimental conditions to perform lactic acid melt polycondensation and interesting findings are reported.

EXPERIMENTAL

Materials

All reagents were ordered from Sigma–Aldrich and used as received. The monomer was an aqueous solution of L(+)-lactic acid (80%). The catalysts tested were tin (II) chloride dihydrate 98% ($SnCl_2$), tin (II) octoate 98% [Sn(Oct)], antimony (III) oxide 99% (Sb_2O_3), zinc acetate dihydrate 98% [Zn(acet)], manganese (II) acetate tetrahydrate 99% [Mn(acet)], tin powder 99.8% (Sn), titanuim (IV) butoxide 97% (TNBT), *p*-toluenesulphonic acid 98% (*p*-TSA), triphenylphosphine 99% (PPh_3), dibutyltin dilaurate 95% (DBTL), tin (II) oxide 99.9% (Sn(II)O), zinc (II) oxide 99% (Zn(II)O), tin (IV) oxide 99.9%, and titanium oxide 99.7% (TiO_2). The solvents, chloroform, HPLC grade chloroform and ethanol, were purchased from Panreac and used without further purification.

Lactic Acid Melt Polycondensation

The experiments were carried out in a 500 mL bench-scale glass vessel equipped with a heating mantle, a mechanical stirrer with a magnetic coupling MRK1/90 and a pressure and temperature control loop. A partial condenser, connected to a vacuum system through a cold trap, allowed removing the byproduct, water, and recycling the monomer and the lactide formed during polymerization, to increase yield. The initial volume of L-lactic acid (200 mL) was introduced in the reaction vessel and allowed to react overnight under inert atmosphere, at increasing temperature and a stirring speed of 600 rpm. The temperature set-point was 170°C. Then, 0.4 wt % of catalyst was added to the reacting mixture (weight of catalyst/initial weight of monomer), the temperature set-point was increased to 180°C and the experiment continued allowing reacting mixture temperature rise for 1 h, before starting the gradual pressure reduction from atmospheric to 10 mbar, which lasted for 7 h. Finally, after reaching the pressure set-point, the reaction system was kept under these conditions for 4 h. At the end of the polymerization, close to 130 g of melt polymer in the form of a brown or light brown viscous melt were poured onto a plate and allowed to cool. Few grams of polymer were purified by dissolution in chloroform and precipitation in 4-fold ethanol and submitted to further characterization. On average, 7% of polymer samples weight was lost as low molecular weight oligomers.

Characterization Techniques

Size Exclusion Chromatography Measurements (SEC).

The average molecular weight (M_w), number molecular weight (M_n) and polydispersity (PD) index were determined by SEC, 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) followed by one PLgel 5μm MIXED-D column (300 × 7.5 mm). The WellChrom Maxi-Star K-1000 HPLC pump from Knauer was set with a flow rate of 0.6 mL min^{-1} and the eluent was HPLC grade chloroform. The measurements were carried out at 25°C with a polymer sample concentration of ~2 mg mL^{-1}, after purification by precipitation. Before the injection (>50 μL), the samples were filtered through a PTFE membrane with a 0.45-μm pore. After column exclusion, the samples were analyzed in an evaporative light scattering detector, PL-EMD 960. Data processing was carried out with GPC Clarity software from DataApex.

Specific Rotation Measurements.

The specific rotation of PLA polymers, $[\alpha]_\lambda^T$, was measured in a AA-5 electrical polarimeter from Optical Activity at 25°C, wavelength of 589 nm and a concentration of 1 g dL^{-1} in chloroform. The percentage of OP of the PLA polymers was calculated using the following relationship[8,16]:

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

where -156[8,16] is the specific rotation of PLA with only L stereoisomer in its composition.

Differential Scanning Calorimetry Measurements (DSC).

Glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and fusion enthalpy (ΔH_m) were measured using a 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 30–180°C temperature range. The percentage of crystallinity (X_c) was calculated using the following relationship[16]:

$$X_c(\%) = \Delta H_m / 93 \times 100$$

where 93 J g^{-1} is the fusion enthalpy[16] of a PLA crystal of infinite size. Universal analysis 2000 software from TA Instruments was used for data processing.

Ultraviolet/Visible Spectroscopy (UV/vis).

UV/vis spectra of polymer samples were obtained from chloroform solutions at room temperature in a Jasco V-550 UV/vis spectrophotometer. The study was performed in the wavelength range from 200 to 800 nm with a scanning speed of 200 nm min^{-1} and a bandwidth of 5 nm.

RESULTS AND DISCUSSION

A large number of works on PLA synthesis by polycondensation, which is a stepwise reaction, are available in the literature[6–18] and some apparently contradictory results have been reported. Polycondensation rate and final polymer molecular weight depend on catalyst performance but also on process scale and on the operating conditions controlling the water vapor diffusion throughout the increasingly viscous polymer bulk and its further withdrawal

Table I. Lactic Acid Melt Polycondensation Results Using Different Catalysts

PLA	Catalyst [0.4 wt %]	M_w [g mol^{-1}]	PD	OP [%]	Yield [%]	Appearance
1	SnCl$_2$	32,500	2.7	77	93	Slightly yellow
2	TNBT	27,000	2.5	76	94	Slightly yellow
3	Sn	39,000	2.1	85	94	Slightly yellow
4	Sn(Oct)	17,000	2.4	82	91	White powder
5	Sb$_2$O$_3$	24,000	2.8	77	85	Slightly yellow
6	Zn(acet)	26,000	2.7	90	80	White powder
7	DBTL	18,000	2.3	89	91	White powder
8	Sn(II)O	18,000	2.3	88	88	Slightly yellow
9	Zn(II)O	16,500	2.4	86	81	Slightly yellow

from the vapor phase.[4,19] Reactor design, including stirring, and temperature and pressure profiles assume special relevance to final polymer molecular weight. In addition, polarity changes in reaction medium have been reported as affecting catalytic activity[16] rendering results comparison rather difficult. Therefore, the experimental work reported here began by assessing catalysts for lactic acid polycondensation under the same melt conditions, followed by studying co-catalysts for the two screened catalysts. The polymerization reaction was performed in a 500 mL bench-scale reactor where pressure and temperature control is available, as well as online record of process conditions, enabling valuable information for process scale-up.

Catalyst Screening

The information on the best catalysts to be screened was gathered from the literature on polyesters synthesis such as PET and PLA.[1,2,5–21] The catalysts used in this study, as well as the results achieved, are compiled in Table I (PLA1–PLA11). The final product from each experiment was investigated by molecular weight distribution measurements, OP and visual appearance, after polymer precipitation from chloroform solutions. According to the data in Table I, catalysts have a dramatic influence on these properties.

The experimental work began by testing SnCl$_2$ (PLA1), a strong Lewis acid largely used in direct lactic acid polycondensation in solution[16,18] as well as in molten state.[7–10] As previously reported,[8] it is a very effective catalyst promoting the synthesis of high molecular weight PLA, but ester interchange reactions are also favored. TNBT is also a Lewis acid and proved to be an efficient polymerization catalyst.[6] However, the final polymer exhibits low OP showing that it is a strong ester interchange catalyst promoting high levels of racemization (PLA2). Tin powder was tested in Experiment 3 and, surprisingly, it allowed the synthesis of the highest molecular weight PLA (39,000 g mol^{-1}) with a relatively high OP (85%). Tin powder has been successfully employed in the lactic acid solution polycondensation[17] but with little success on melt polycondensation.[14,15] Tin powder requires an additional purification step to remove this catalyst from the final polymer bulk, which may explain the interest in other tin-based compounds. In applications in the commodity field the purification stage may jeopardize process cost balance. Nevertheless, in biomedical applications, where high purity PLA grades are mandatory, purification may be always required ensuring avoiding cytotoxicity problems. In

addition, it has been reported[22] that the complete removal of residual catalysts enhances the polymer melt stability during subsequent melt processing stages. Therefore, purification requirements may not be always envisaged as a limitation to proceed with catalyst testing. In Experiment 3, when using tin metal, right after turning off the heating the catalyst solidified in aggregates (Figure 1) that were easily removed from the reactor bottom allowing recovering the catalyst. This unexpected observation may be related to the catalyst melting point, within reaction temperature range.

Tin (II) octoate, [Sn(II)Oct], a strong Lewis acid, is the catalyst usually employed in the ROP process[1,20] and was also reported by Hiltunen et al. as an efficient lactic acid melt polycondensation catalyst.[12] Nevertheless, under the conditions tested in this work, it did not lead to encouraging results (PLA4). Antimony oxide (Sb$_2$O$_3$) and zinc acetate [Zn(acet)], both widely used in the PET synthesis by melt polytransesterification and polycondensation,[4,5] were tested in Experiments 5 and 6, respectively, showing low catalytic activity toward lactic acid melt polycondensation. However, it is worth mentioning that zinc acetate allowed synthesizing the polymer (PLA 6) with higher OP (90 %) and may be preferred on account of stereoregularity, when relevant. Other standard esterification catalysts such as DBTL, Sn(II)O, and Zn(II)O were also tested in Experiments 7–9, respectively, leading to similar results, which are not very encouraging for lactic acid melt polycondensation. A few other compounds mentioned in the literature[5,12] as efficient polycondensation catalysts such as tin (IV) oxide, titanium (IV) oxide, sulphuric, and phosphoric acid were also assessed. Results not
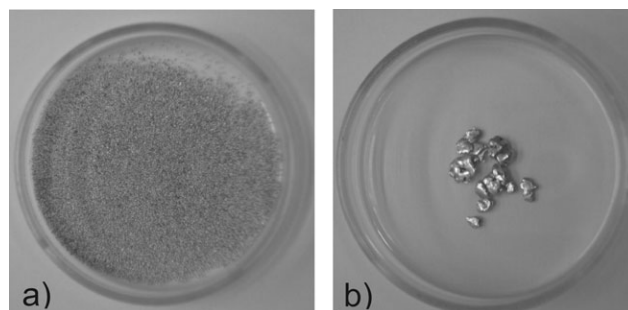

Figure 1. Visual appearance of tin metal catalyst before (a) and after polymerization (b).

Table II. Lactic Acid Melt Polycondensation Results Employing Co-Catalysts

PLA	Catalyst [1 mol %]	M_w [g mol^{-1}]	PD	OP [%]	Yield [%]	Appearance	Torque [Ncm]
10	Sn/p-TSA	37,000	3.2	86	81	White powder	5.4
11	Sn/PPh$_3$	35,000	3.3	91	83	White powder	3.3
12	SnCl$_2$/p-TSA	52,000	1.4	83	73	White powder	30
13	SnCl$_2$/PPh$_3$	52,000	1.3	81	77	White powder	20

shown here revealed a low catalytic activity of these chemicals toward lactic acid polycondensation, therefore not included in this discussion. The results above, Table I, clearly illustrate that different catalysts produce different polymers in terms of molecular weight and stereoregularity which should be taken into account when planning further studies. Yield is another important criterion to assess a process, therefore included in Table I and calculated using eq. (1):

$$Yield(\%) = \frac{\text{Weight of product}}{\text{Weight of monomer} \times 0.8} \times 100 \qquad (1)$$

while assuming each mole of monomer releases one mole of water. The yields in Table I are all above 80%, quite high for melt polycondensation reactions,[23] and slightly dependent on the catalyst.

The colour of the final materials ranged from white to a pale yellow powder, depending on the catalyst, suggesting the occurrence of thermo-oxidative degradation reactions, besides racemization. The polyester's color is an important quality parameter and therefore has been used for qualitative assessment while checking the catalyst performance. The last column in Table I describes the appearance of the polymers, explained in more detail later. However, it can be already pointed out that the results do not suggest a clear relationship between polymerization rate, OP and color formation, not even whether these are competitive phenomena or not. Therefore, these parameters will be analyzed separately in the following sections taking only into account the catalyst influence.

Co-Catalysts

In the catalyst screening stage, tin chloride (SnCl$_2$) and tin powder (Sn) (Experiments 1 and 2) were assessed as the most efficient catalysts and therefore selected for further experiments. Nevertheless, as referred before, these catalysts also favor side reactions leading to melt polymer yellowing and racemization. Aiming at overcoming this and following Moon and Kimura, 2003 and Degée et al. 1999 works, in a second set of experiments two co-catalysts were tested (PLA10 to PLA13 in Table II). These two co-catalysts, added to the catalyst in an equimolar ratio, were P-TSA,[7] a protonic acid, and PPh$_3$,[20] a Lewis base.

The results in Table II reveal major differences regarding the catalysts' performance in the presence of these two compounds. The addition of a co-catalyst to neat tin powder (PLA10 and PLA11) does not significantly influence the polymerization degree, but the addition of PPh$_3$ (PLA11) allowed the synthesis of the highest (91%) OP polymer. On the other hand, when

added to SnCl$_2$ (PLA12 and PLA13) they accelerated the rate of polymerization. Indeed, the molecular weight reached when using SnCl$_2$ combined with co-catalysts increased from 32,500 to 52,000 g mol^{-1}, together with a narrower molecular weight distribution and a slightly higher OP, regardless the co-catalyst employed. Thus, in general, it can be stated that these co-catalysts enforce a better controlled polymerization leading to a higher OP polymer, while reducing yellowing. The role of these compounds while improving polymerization reactions is still under discussion. It has been proposed that they lead to the formation of complex metalloxy compounds and then the polymerization proceeds on the tin-oxygen bond of the alkoxide ligant.[7,19,20] In the particular case of SnCl$_2$/p-TSA catalytic system,[7] a mechanism has been put forward by Moon et al. 2000.

It is worth mentioning that racemization reactions occur whatever the catalytic system used and cannot be completely prevented, as the OP results in Tables I and II show. The occurrence of racemization reactions, previously identified in ROP and melt/solution polycondensation mechanisms,[12,16,20] are responsible for the random introduction of 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[12,24] and, therefore, will not be discussed here.

At large-scale polyesters production, the viscosity plays an important role being often selected for inline monitoring by measuring torque in the stirring system. This is a very good method for melt viscosity estimation as it is correlated with average molecular weight. The addition of these co-catalysts also affects the polymer melt viscosity and therefore torque measurements were recorded during the last experiments. Figure 2 shows the torque progress during the overall reaction from monomer distillation to the final polymerization stage, after catalytic system addition, which was SnCl$_2$ combined either with p-TSA, Experiment 12 (full dots), or with PPh$_3$, Experiment 13 (empty dots). The melt viscosity curves depict a slow increase in torque while molecular weight is low, less than $\approx$ 30,000 g mol^{-1}, and an exponential increase as polymer chain grows further. The high viscosity of PLA in the later stages of the melt polycondensation process hinders water removal and therefore limits the final molecular weight achieved with this process. Nevertheless, as it stands out in Figure 2, the use of PPh$_3$ allows a significant melt viscosity reduction close to the end of the process and may be regarded as an advantage to p-TSA.

Thermal Characterization

Information on the thermal behavior is relevant for evaluating the physical properties of semi-crystalline polymers, the data
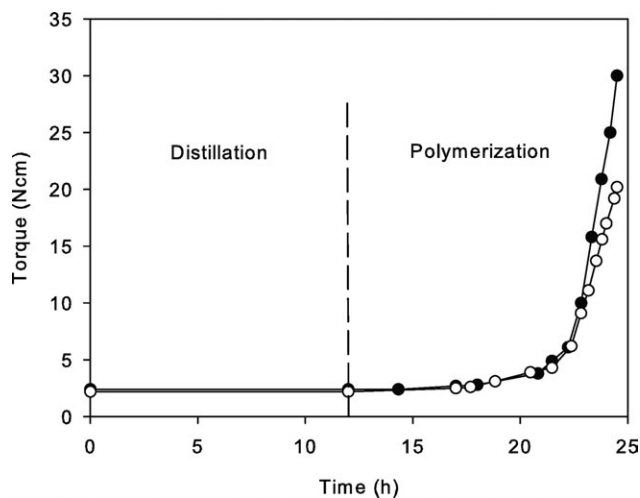
Figure 2. Torque measurement during Experiments 12 (full dots) and 13 (empty dots) using different co-catalysts (p-TSA and PPh3) together with SnCl$_2$.

summarized in Table III were achieved by DSC analysis. The glass transition temperature, T_g, and crystallization temperature, T_c, were obtained from the second heating scan, whereas the melting temperature, T_m, and fusion enthalpy, employed to assess crystallinity degree, were obtained from the first heating scan.

It is easily observed that the thermal properties of the samples greatly differ from each other, ranging from semi-crystalline (PLA3-8 and PLA10-13) to amorphous behavior (PLA1, PLA2, and PLA9). Glass transition and melting temperatures are regarded as highly dependent on molecular weight. However, in the data recorded in Table III this trend is not clear. The glass transition temperature ranges from 36°C to 55°C, the crystallization temperature from 90 to 110°C and the melting temperature ranges from 131°C to 156°C. These temperatures are lower than those reported for commercial polylactides[25] but are in good agreement with previous results for PLA[11–13] in the same
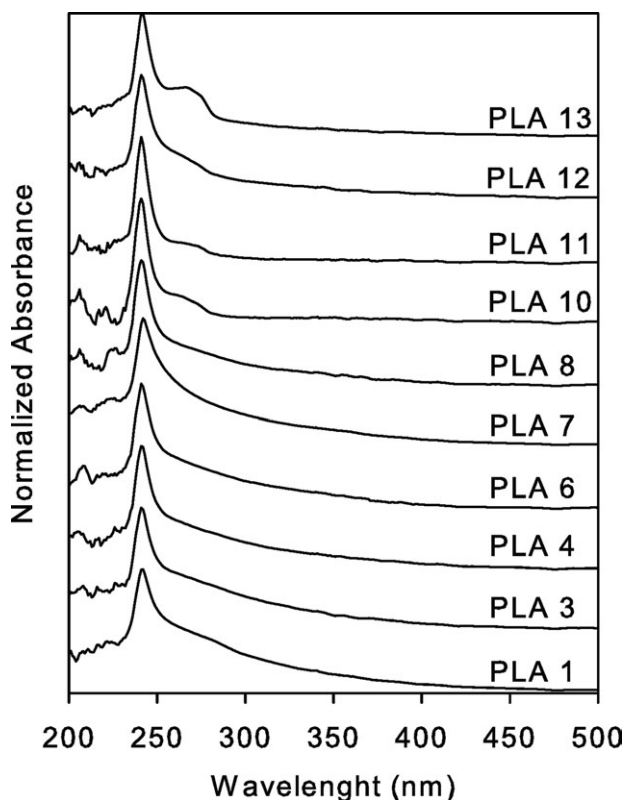

Figure 3. Ultraviolet–visible spectra of PLA samples.

molecular weight range, also produced by lactic acid polycondensation.

In general, the crystallinity degree data in Table III, show a close correlation with the OP as polymers with the highest crystallinity degree also exhibit the highest OP (PLA6, PLA8, and PLA11). It is well known[12,25] that PLA stereoregularity strongly influences its crystallinity and thermal behavior, which may
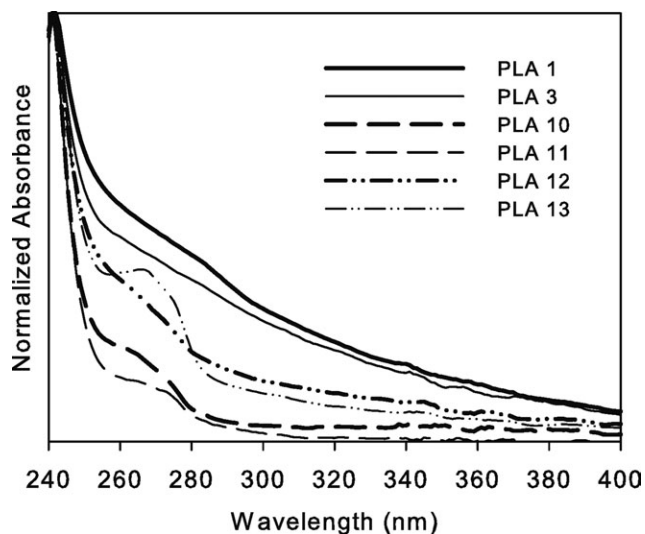
Table III. Thermal Characterization of the Polymer Samples

PLA	T_g [°C]	T_c [°C]	T_m [°C]	X_c [%]
1	–	–	–	–
2	–	–	–	–
3	55	–	156	36
4	48	108	142	36
5	–	–	138	35
6	54	110	152	46
7	–	–	141	29
8	53	103	153	49
9	–	–	–	–
10	–	90	135	24
11	45	102	143	43
12	36	–	134	41
13	41	–	131	34

Figure 4. Ultraviolet–visible spectra of some PLA samples in the 240–400 nm wavelength region.

explain the unexpected trend between molecular weight and thermal characterization results discussed above. According to Hiltunen et al. 1997, the D-lactyl units, introduced due to racemization reactions, prevent the crystallization process.

Yellowing

The OP results in Tables I and II and the slightly yellowish coloration of some polymer samples undoubtedly suggest the occurrence of undesirable degradation reactions during the melt lactic acid polycondensation. The OP decrease is related to transesterification reactions[12,24,25] and the colour change is ascribed to the formation of chromophores due to thermo-oxidation reactions.[26,27] It is clear that the addition of the co-catalysts considered in this work hinders the colour formation and transesterification reactions to some extent (PLA10 to 13) as the samples are now white and the OP slightly increased.

Since the visual examination of the polymer samples after purification is rather subjective, UV/vis spectroscopy was employed to enable identifying which catalyst has a stronger influence upon colour formation, as well as the role of the co-catalyst. The literature confirms that UV/vis spectroscopy has been successfully applied to follow the effect of melt processing on the properties of PLA[28] and also the effect of ionizing radiation on thermoplastic polymers such as PET, LDPE and polyamides.[29] Surprisingly, so far it has not been used to assess lactic acid polymerization, although it is a unique technique allowing highly sensitive detection of traces of chromophores.

The ultraviolet–visible spectra of PLA samples dissolved in chloroform and measured in the wavelength region from 200 to 500 nm are presented in Figure 3. Above 500 nm, no absorbance was recorded. All spectra show a maximum absorbance peak at 240 nm and, according to Garlotta,[1] this is attributed to the ester group present in the polymer main chain. After this maximum absorbance peak, and increasing wavelength, all spectra depict a continuous decrease in absorbance which, in some cases, extends to the visible region of the spectrum. UV/vis spectroscopy was previously used by Wang et al. 2008 to study the effect of melt extrusion conditions on PLA thermal degradation in the range of 300–1000 nm, and a similar behavior was observed. This absorption tail was ascribed to the creation of chromophores during melt processing, small amounts of conjugated double bonds with carbonyl groups, which are responsible for the perceived polymer colour.[26–28,30]

In the low wavelengths region, from 200 to 240 nm, small absorbance peaks are exhibited in every spectrum. These peaks are assigned to the hydroxyl and carboxyl end groups. However, owing to the high noise in this spectral region, the small peaks registered will not be considered here.

To deepen the understanding of the influence of co-catalysts upon polymerization, Figure 4 shows the enlarged absorbance profiles of PLA1 and PLA3 synthesized with SnCl$_2$ and tin powder (see Table I), and PLA10 to PLA13, obtained by adding co-catalysts (see Table II).

The results in Figure 4 enlighten that the absorption intensity decreased both with PPh$_3$ and p-TSA addition to the initial catalyst. This supports the fact that these co-catalysts hinder thermal degradation reactions, and is in agreement with the change in polymer samples colour. The shift for lower intensities is much more evident when tin powder is the catalyst, irrespectively of the co-catalyst under consideration. When using SnCl$_2$ combined with co-catalysts, the absorption intensity is significantly higher than for PLA10 and PLA11, but still lower than when co-catalysts are not added.

CONCLUSION

Catalysts screening was the first stage in this work on PLA synthesis by lactic acid melt polycondensation and tin powder and SnCl$_2$ were selected as the most efficient catalysts. Samples' characterization revealed that, besides polymerization, these catalysts also allowed racemization and thermo-oxidation reactions which could be better controlled by using a suitable co-catalyst. The addition of PPh$_3$ or p-TSA had a remarkable effect on molecular weight, OP, colour, and even on polymer melt viscosity, allowing the synthesis of PLA polymers with enhanced properties. Thus, the catalytic system selection for PLA production may be based on the target molecular weight, purity grade and the requirement of an accurate control over stereoregularity.

The development of colour in the later stages of melt polymerization limits the polymerization time and therefore contributes to reducing the advantages of using this process for large-scale PLA production. Minimization of degradation during melt polycondensation and improved role of commonly tin-based catalysts will be a major asset enabling developing a more cost effective process for commercial production of PLA. Further studies are crucial to obtain high-molecular weight PLA by lactic acid melt polycondensation, up to 100,000 g mol^{-1}, without compromising its quality.

ACKNOWLEDGMENTS

REFERENCES

1. Garlotta, D. *J. Polym. Environ.* **2002,** *9*, 63.

2. Gupta, A. P.; Kumar, V. *Eur. Polym. J.* **2007,** *43*, 4053.

3. Smith, R. Biodegradable Polymers for Industrial Applications; Woodhead Publishing Limited: Cambridge, **2005.**

4. Scheirs, J.; Long, T. E. Modern Polyesters: Chemistry and Technology of Polyesters and Copolymers; Wiley & Sons: West Sussex, **2003.**

5. Pang, K.; Kotek, R.; Tonelli, A. *Prog. Polym. Sci.* **2006,** *31*, 1009.

6. Chen, G.-X.; Kim, H.-S.; Kim, E.-S.; Yoon, J.-S. *Eur. Polym. J.* **2006,** *42*, 468.

7. Moon, S.-I.; Lee, C.-W.; Miyamoto, M.; Kimura, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2000,** *38*, 1673.

8. Moon, S.; Kimura, Y. *Polym. Int.* **2003,** *52*, 299.

9. Moon, S.-I.; Lee, C.-W.; Taniguchi, I.; Miyamoto, M.; Kimura, Y. *Polymer* **2001,** *42*, 5059.

10. Moon, S.; Taniguchi, I.; Miyamoto, M.; Kimura, Y.; Lee, C. *High Perform. Polym.* **2001,** *13*, S189.

11. Sedlarik, V.; Kucharczyk, P.; Kasparkova, V.; Drbohlav, J.; Salakova, A.; Saka, P. *J. Appl. Polym. Sci.* **2010,** *116*, 1597.

12. Hiltunen, K.; Seppala, J.; Harkonen, M. *Macromolecules* **1997,** *30*, 373.

13. Hiltunen, K.; Seppala, J. V. *J. Appl. Polym. Sci.* **1998,** *67*, 1011.

14. Zhao, Y.; Wang, Z.; Wang, J.; Mai, H.; Yan, B.; Yang, F. *J. Appl. Polym. Sci.* **2004,** *91*, 2143.

15. Nagahata, R.; Sano, D.; Suzuki, H.; Takeuchi, K. *Macromol. Rapid Commun.* **2007,** *28*, 437.

16. Marques, D. A. S.; Jarmelo, S.; Baptista, C. M. S. G.; Gil, M. H. *Macromol. Symp.* **2010,** *296*, 63.

17. Ajioka, M.; Enomoto, K.; Suzuki, K.; Yamaguchi, A. *Bull. Chem. Soc. Jpn.* **1995,** *68*, 2125.

18. Kim, K. W.; Woo, S. I. *Macromol. Chem. Phys.* **2002,** *203*, 2245.

19. Maharana, T.; Mohanty, B.; Negi, Y. S. *Prog. Polym. Sci.* **2009,** *34*, 99.

20. Degée, P. H.; Dubois, P. H.; Jacobsen, S.; Fritz, H.-G.; Jérôme, R. *J. Polym. Sci. Part A: Polym. Chem.* **1999,** *37*, 2413.

21. Marques, D. S.; Gil, M. H.; Baptista, C. M. S. G. *J. Appl. Polym. Sci.* **2012,** *125*, E283.

22. Fan, Y.; Nishida, H.; Shirai, Y.; Endo, T. *Polym. Degrad. Stab.* **2004,** *84*, 143.

23. Achmad, F.; Yamane, K.; Quan, S.; Kokugan, T. *Chem. Eng. J.* **2009,** *151*, 342.

24. Chabot, F.; Vert, M. *Polymer* **1983,** *24*, 53.

25. Tsuji, H.; Ikada, Y. *Macromol. Chem. Phys.* **1996,** *197*, 3483.

26. Ciolacu, F. C. L.; Choudhury, N. R.; Dutta, N. *Polym. Degrad. Stab.* **2006,** *91*, 875.

27. Ciolacu, F. C. L.; Choudhury, N. R.; Dutta, N.; Voelcker, N. H. *Macromolecules* **2006,** *39*, 7872.

28. Wang, Y.; Steinhoff, B.; Brinkmann, C.; Alig, I. *Polymer* **2008,** *49*, 1257.

29. Moura, E. A. B.; Ortiz, A. V.; Wiebeck, H.; Paula, A. B. A.; Silva, A. L. A.; Silva, L. G. A. *Radiat. Phys. Chem.* **2004,** *71*, 199.

30. Carrasco, F.; Pagès, P.; Gámez-Pérez, J.; Santana, O. O.; Maspoch, M. L. *Polym. Degrad. Stab.* **2010,** *95*, 116.