Study of the Polymerization Kinetic of Lactic Acid

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Summary: Biodegradable polymers production is growing, mainly poly (lactic) acid, due to the fact that it is environmentally friendly and might be used in different fields i.e. medicine, agriculture, textiles, etc. Hence the importance of studying the polymerization process and its kinetic parameters. The polymerization process is performed by polycondensation of lactic acid using different kinds and amounts of tin based catalysts. This process is monitored during 12 hours and samples are taking for analyses every hour. Each sample is measured by gel permeation chromatography (GPC) to determine its molecular weight and by Fourier transformed infrared (FTIR) to study the evolution of alkyl absorption bands and the disappearing of hydroxyl ones. Modulated differential scanning calorimetric analysis (MDSC) is used to study the thermal behavior of every sample during each period, such as *Tg* displacement and changes in crystallization and melting. These data are used for the construction of the kinetic curve.

Keywords: biopolymers; gel permeation chromatography; polycondensation; polylactic acid; thermal properties

Introduction

Conventional polymers have many applications, but they cause an environmental problem due to the fact that they do not degrade in reasonable time and they generate a high volume of solid residue after having been used, therefore biodegradable polymers are an important alternative[1,2]

Polylactic acid or polylactide (PLA) is a biodegradable polymer with good properties, such as mechanical strength, transparency, compostability, environmental safety and biocompatibility. Other great advantage of PLA is that it is produced from lactic acid (LA), which can be obtained from renewable resources such as corn or sugar beets.[3]

PLA, with high average molecular weight has a high cost as a consequence of the several steps involved in the polymerization process. It can be produced by ring opening polymerization or azeotropic condensation, the former has several steps where the first step involves the formation and purification of lactide from the oligocondensates of LA and then the formation of PLA. In azeotropic condensation lactic acid and catalyst are azeotropically dehydrated in a refluxing high-boiling aprotic solvent under reduced pressure.[4,5]

PLA can be also obtained by using catalyzed melt condensation of lactic acid, however, the polymer obtained through this procedure has low molecular average weight because it is difficult to obtain high molecular weights in a solvent-free system, but it has the advantage, that the polymer has a low cost. If high molecular weights and better mechanical properties are required it is necessary to use coupling agents or esterification-promoting adjuvants, but these increase the costs, furthermore is necessary to use dangerous or flammable solvents, and the procedure requires additional purification or separation. These additives are not biodegradable or bioabsorbable.[4]

For biomedical and agricultural applications such as controlled solutes delivery

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PLA with low molecular weights are generally preferred, because they are degraded in the human body or in the soil faster than PLA of high molecular weights,[6,7] besides, these applications do not require high mechanical properties.

In catalyzed melt polycondensation, proper selection of a catalyst is very important, because it activates the dehydrating reaction, deactivates the formation of lactide and increases the final molecular weight. It is also important to consider that the catalyst activity can change during the polycondensation reaction since the polarity of the reaction system is greatly altered. At the beginning, LA and its primary condensates have high polarity since they all contain both carboxyl and hydroxyl groups in a high ratio, whereas the final PLA consisted of less polar ester groups, leading to a great decrease in polarity, then it is important to add the catalyst after dehydration of LA and the formation of oligo(lactic acid).[8]

Discoloration of PLA caused by degradation has been a serious problem in the polycondensation process. It might be caused by various factors, such as high reaction temperatures, long reaction times, catalysts, solvents, and side reactions. The degradation is noted by color changes from yellow to brown, and finally to black. In order to prevent degradation and increase the molecular weight, the addition of protic acids such as boric acid, methaphosphoric acid and p-toluenesulfonic acid monohydrate (pTSA) is recommended. Additionally, the pTSA prevents side reactions, stimulates the dehydration and increases reaction rate.[8–10]

On the basis of the above considerations, we study the influence of the type and amount of catalysts in presence of a protic acid, and its effect on the molecular weight, thermal transitions and polymerization kinetics of PLA obtained by catalyzed melt polycondensation.

Experimental Part

Materials

(D,L) Lactic acid (LA) reagent grade with a 85 wt% of purity, stannous chloride ($SnCl_2$) and stannous octoate ($Sn(Oct)_2$) were obtained from MP Biomedicals Inc, p-toluenesulfonic acid, chloroform and methanol were purchased from Merck. All reagents were used as received.

PLA Synthesis

This procedure was carried out on two steps, dehydration and polycondensation. The dehydration was performed with continuous magnetic stirring and refluxing at 60 °C for 3 hours, under reduced pressure by using a vacuum pump, to avoid lactic acid degradation and lactide sublimation, without using any drying agent

In order to begin the polycondensation step, different ratios of catalysts (pTSA, $SnCl_2$, $Sn(Oct)_2$) were weighed according to the amount of dehydrated lactic acid, then they were blended together with continuous magnetic stirring under reduced pressure, until reaching the target temperature (165 °C), temperature was increased gradually to avoid lactic acid decomposition and to generate oligomeric species that tolerate higher temperatures. When the time reaction was completed the samples were purified dissolving them in chloroform and then they were precipitated by using methanol and finally they were filtered and dried to obtain the polymer as a powder.

Methods

The molecular weights were determined by Gel Permeation Chromatography (GPC) on a Waters equipment using two columns, Styragel® HT 6E and Waters StyragelTM HR 4E, placed in series and operated at a flow rate of 0.4 ml/min in tetrahydrofuran at 27 °C, and equipped with refractive index detector. The molecular weights were obtained using a calibration curve built from polystyrene standards. Due to the high dependence of molecular weight with analysis conditions, for instance a change of 0,1 mL/min in flow rate produces differences of 10% on molecular weight measurement, several trials were conducted to establish the optimal working parameters.

Modulated differential scanning calorimetric (MDSC) TA Instrument Q100 was used to obtain glass transition temperatures (Tg), melting points (Tm), crystallization temperatures (Tc) and melting heats, and other thermal transitions, this procedure was performed using the fastest heating ramp to reach 190 °C and the fastest cooling rate to −50 °C to erase the thermal history, then the heating rate was modulated ±1 °C every minute with a ramp 2 °C/min to 200 °C.

Infrared spectra were obtained from a FTIR spectrometer Perkin Elmer Spectrum One model, by using casted films of the polymer in a SeZn cell.

Results and Discussion

Polymerization

Several experiments were made in order to optimize the catalytic system and reaction temperature; during these tests we observed that when the reaction was carried out without pTSA at any temperature, or when the heating rate was too fast or when the reaction temperature was higher than 165 °C after 3 hours, the reaction product was carbonized, this happened because the polycondensation process needs the oligomeric species to increase their molecular weight so that they can tolerate the increasing temperature.[12] Then pTSA was added to promote the formation of oligomeric species, due to its catalytic acid character in condensation reactions.[8,9,11]

The polymerization conditions were optimized at 165 °C, 800 Pa and using 1 wt% of catalyst respect to dehydrated lactic acid. Table 1, shows different catalyst ratios $SnCl_2/Sn(Oct)_2$ used for the PLA synthesis, in presence of constant pTSA amount.

It is known that during the polycondensation process of lactic acid, lactide is produced, due to side reactions, such as depolymerization and fragment cyclization.[4]

The polymerization yields confirm the lactide production. The high polycondensation yields gave low lactide production and samples with minor polymerization yields gave high lactide amount as is shown in Table 2. We can conclude that the lactide formation in this reaction depends on the catalyst used. For samples 1, 2 and 4 low lactide amount is observed, but the rest of the samples had a considerable amount of lactide, sample 5 having the highest lactide formation, this could be explained because $Sn(Oct)_2$ catalyst under specific reaction conditions produces the polylactide[13] and the low lactide formation can be explained due to the fact that $SnCl_2$ promotes the direct polycondensation reaction as it has been reported in previous works.[10,14] It is important to highlight that low reaction yields were also caused by degradation, because the final polymer was colored and after purification, as depicted before, the color disappears, due to the fact that degraded fragments were eliminated.

GPC Characterization

Figure 1 shows the growth of weight-average molecular weight $\langle M_w \rangle$ with reaction time for all of catalytic systems at 165 °C during 10 hours. At the beginning of the reaction the main differences are observed, samples 3 and 5 at 1 hour of

Table 1.
Catalytic Systems.[a]

Sample	$SnCl_2$	$Sn(Oct)_2$	pTSA	Ratio	Total Sn
	wt%	wt%	wt%	$SnCl_2/Sn(Oct)_2$	wt%
1	50	0	50	1:0	26
2	37,5	12,5	50	3:1	23
3	25	25	50	1:1	20
4	12,5	37,5	50	1:3	18
5	0	50	50	0:1	15

[a] 1 wt% of catalytic systems respect to dehydrated lactic acid was used in the reactions.

Table 2.
Sample appearance and polymerization yield percent.

Sample	Yield (wt%)	Color before purification	Color after Purification
1	54	Light brown	White
2	40	Light brown	White
3	37	Yellowish	White
4	46	Yellowish	White
5	32	Brown	White

reaction had lower $\langle M_w \rangle$ than samples 1, 2 and 4. This behavior is associated with the catalytic system because samples with higher $SnCl_2$ quantity increased their $\langle M_w \rangle$ faster, due to the fact that this catalyst presents better performance to form oligomeric species by polycondensation in the first stages of the reaction, where $Sn(Oct)_2$ catalyze the lactide formation,[1,4,13] that is why on first steps of the reaction there is not a great increment on $\langle M_w \rangle$, Figure 1 right side, but after the lactide is formed, the polymerization proceeds and $\langle M_w \rangle$ rises.

From Figure 1, it can be seen that the sample 1 until the 7th hour showed a constant increment in $\langle M_w \rangle$, but then $\langle M_w \rangle$ decreases, this can be associated with a polymer degradation or depolymerization, catalyzed by $SnCl_2$, it was confirmed experimentally, because after 8 hours of reaction, the polymer acquired a brown coloration.

The fluctuating behavior of samples 1 and 2 can be explained taken into account that $SnCl_2$ catalyst can cause degradation or depolymerization, causing strong changes on Mw during the reaction.[8,14,15] This behavior had not been reported, because in previous works the time between sample recollections was too long.

Sample 3 presents fluctuations on $\langle M_w \rangle$ and then there is a stable increment on Mw that can be associated with $Sn(Oct)_2$ role, as seen in samples 4 and 5; The behavior of sample 4 also depends on the catalyst type and amount, $SnCl_2$ presence causes a high $\langle M_w \rangle$ the 1st hour and decomposition after the 7th hour, but it also has a very constant increment in $\langle M_w \rangle$, characteristic of $Sn(Oct)_2$.

Table 3 shows the polydispersity index (PDI) obtained from different samples; there is not an appreciable difference among them, which indicates that the catalyst nature does not have influence on broadness of molecular weight distribution, or polymer chain length. The PDI value is close to 2 and to this kind of systems indicates that the polymerization degree is almost 1 at the end of the reaction since $PDI = 1 + p$, where p is the conversion.[16]

MDSC Characterization

All samples show similar thermal behavior, Figure 2 shows typical reversible and non reversible thermograms of MDSC run. In the reversible thermogram, the glass transition temperature (Tg) appears and a broad reversible endothermic peak for the melting of PLA. In the non-reversible thermogram an endothermic peak related to the relaxation of macromolecules, because these macromolecules are frozen at the glassy state in a non favorable conformation, and a sharp peak is observed just

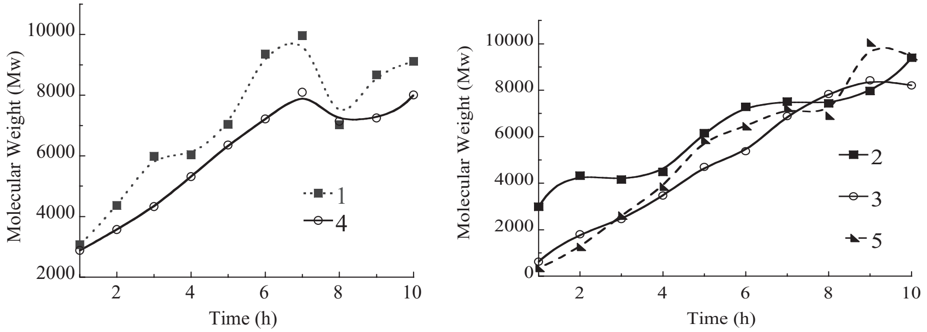

Figure 1.
Weight-average Molecular Weight $\langle M_w \rangle$ variation with time.

Table 3.
Final polydispersity of samples.

Sample	Mw	Mn	PD
1	9116	4898	1,9
2	9398	5281	1,8
3	8203	4473	1,8
4	8008	3877	2,1
5	9464	4757	2,0

Table 4.
Thermal transitions of PLA samples.

Sample	Tg(°C)	Tm(°C)	Tc(°C)	$\Delta_m H$ (J/g)
1	53,39	148,17	83,60	30,98
2	41,34	133,38-144,95	81,23	18,34
3	32,95	139,34	75,09	15,68
4	34,86	137,61	74,02	17,97
5	51,34	148,46	80,26	29,54

before *T*g, which is attributed to a cold crystallization of PLA, and endothermic peak assigned to a transesterification or decomposition of the polymer.

Table 4 shows the thermal transitions for each sample. *T*gs for samples 1 and 5 are the highest, hence both polymers have the molecular weight distribution quite similar (Mw are almost equal, see Figure 3). Although sample 2 molecular weight distribution is similar to those of sample 1 and 5, its *T*g is lower than the last ones mentioned, but this sample show two melting points, which indicates there are two crystalline phases or two crystallite sizes that are changing the chain mobility. Samples 3 and 4 have a very similar $\langle M_w \rangle$ and hence they have a comparable *T*g value. The same tendency was observed for *T*m and *T*c.

Melting enthalpy ($\Delta_m H$) indicates the degree of crystallization of PLA which depends on the stereochemistry of the lactic acid used. In this case a racemic lactic acid was employed, it can be seen that $\Delta_m H$ is higher for sample 1 and 5, which could mean that each catalyst alone favors a different reaction pathway. Since, the D and L lactic acid are present in the system, the sequence of D and L units on the polymer determine the tendency to crystallize, that is reason why binary mixtures of $SnCl_2$ and $Sn(Oct)_2$ are used crystallization degree decreases, because the order of D and L units on polymer chain changes, and its ability to crystallize diminishes. The characterization of each sample to know the stereochemistry of PLA will be subject of a future paper.

IR characterization

Every sample presents the same absorption bands on IR spectra. Figure 4 shows FTIR spectra for sample 2 at different reaction times. A qualitatively analysis of absorption bands with reaction time, shows a decrease in the intensity of the –OH band, which indicates that end groups decrease due to the polycondensation reaction progress.

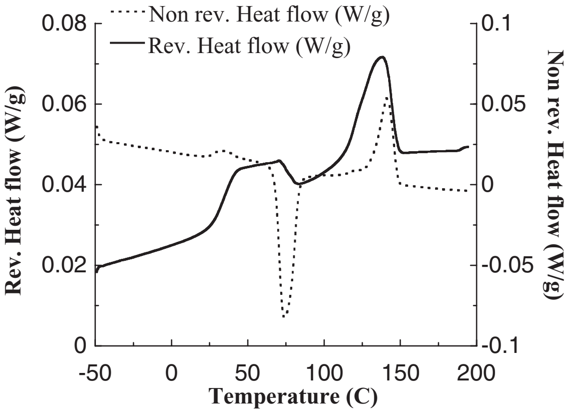

Figure 2.
Typical MDSC run. Sample 4.

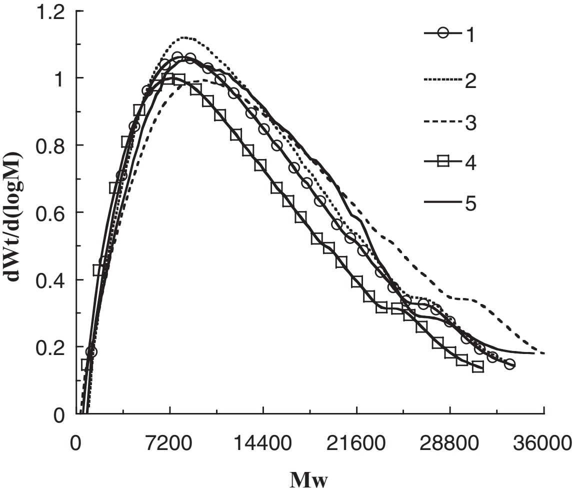

Figure 3.
Molecular weight distributions of PLA samples.

Kinetics
By using data obtained from GPC measurements, the polymerization degree (*X*n) was calculated, taking into account that *X*n is the ratio between $\langle M_w \rangle$ and *Msu*, where *Msu* is the molecular weight of structural unit of PLA.

As it was discussed above, samples 1 and 4 shows a decrement on $\langle M_w \rangle$ after 7 hours, that is the reason why data from the first to the 7th hour were used to build the kinetic curves (*X*n vs time), because there are side reactions such as depolymerization or degradation that were not taken into account in the kinetic model used.[17] In the other samples all data were used.

Figure 5 illustrates the kinetic curves for each PLA samples, corresponding to external catalyst kinetic model,[16] it is clearly observed that there is linear relationship between Xn and time and a good linear fitting of data as can be seen on correlation

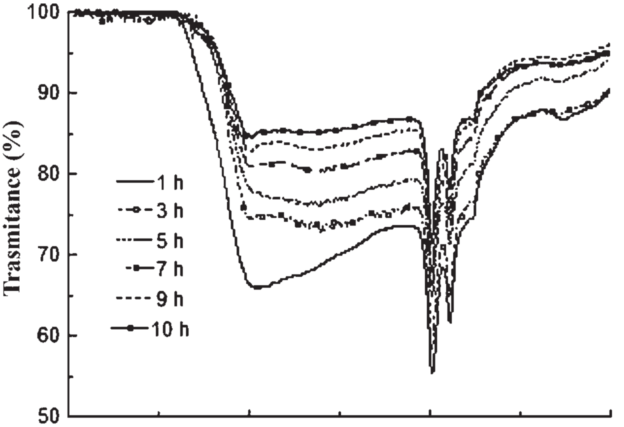

Figure 4.
IR spectra of PLA at different times.

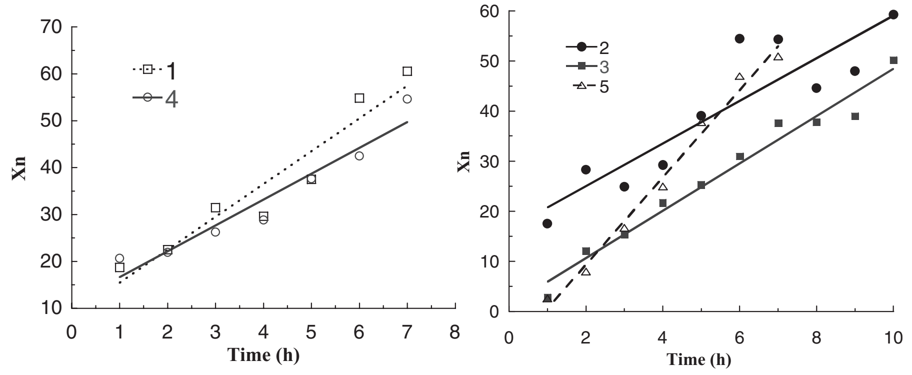

Figure 5.
Polymerization kinetics of PLA.

coefficient values on Table 5, this behavior is expected since the polymerization was done using a catalyst that increases the polymerization degree.[17]

Table 5 shows the slope of fitted kinetic curves, which are called rate constants, because it is proportional to the polymeric chains length increment with time. Rate constants values for pure catalyst ($SnCl_2$ or $Sn(Oct)_2$) are the highest ones, which indicates that there is an effect of catalyst nature on polymerization kinetic, because there is a change in reaction mechanism. The samples with high $Sn(Oct)_2$ content have higher velocity constant values than the others. The velocity constant for samples 2, 3 and 4 seems to be a function of catalyst ratio.

Conclusions

It was found that the $\langle M_w \rangle$ of the polymerizations studied after 10 hours reaction time are almost independent of the catalytic system used, because all the samples show a comparable value at this time, but the tendency of $\langle M_w \rangle$ with time varies with each catalytic system. The samples with higher $SnCl_2$ content have the more fluctuant behavior during reaction. The catalytic system with higher $Sn(Oct)_2$ quantity shows a very steady behavior in Mw with time and also more tends to produce more lactide.

Table 5.
Kinetic data.

Sample	Correlation coefficient	Rate constant
1	0,92	7,01
2	0,81	4,26
3	0,97	4,73
4	0,93	5,51
5	0,99	8,71

The thermal transitions behaved according to molecular weight distribution, because the samples with high number of large polymer chains had the highest values on thermal transitions.

According to the analysis done about the crystallization degree, $SnCl_2$ and $Sn(Oct)_2$ produce a different order of the D and L lactic acid units on the polymer backbone.

The reaction kinetic is very dependent on the nature of the catalyst, it was seen that $Sn(Oct)_2$ alone presents the highest velocity constant.

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