

L-Lactide Polymerization in the Presence of Gaseous Nitrogen

Polimerização do L-lactídeo na Presença de Nitrogênio Gasoso

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Abstract

During the ring opening polymerization of L-lactide the presence of water must be avoided since even small amounts can influence negatively on the reaction kinetic behavior. An effective way of removing water from the reaction system should be easy to implement and have comparatively low cost. The objective of the work was to obtain poly (L-lactic acid) at different conditions of temperature and catalyst concentration when gaseous nitrogen is used to purge the reactor comparing the resulting conversion profiles and final average molar masses. Results showed that a long induction period was observed when no gaseous nitrogen was used. It suggests that nitrogen was effective in removing the water from the reaction system since induction periods were not observed when it was injected before polymerization. Depolymerization was avoided when gaseous nitrogen was used resulting in higher molar masses than the case when no purging was carried out.

Keywords: Biopolymer. Depolymerization. Gaseous Nitrogen. PLLA. Poly(L-lactic acid). Ring Opening Polymerization.

Resumo

A presença de água durante a polimerização por abertura de anel de L-lactídeo deve ser completamente evitada. Mesmo presente em pequenas quantidades, a água pode influenciar negativamente o comportamento cinético da reação. A remoção da água de maneira eficaz, a partir do sistema de reação, deve ser de fácil aplicação e com custo relativamente baixo. O objetivo deste trabalho foi obter poli(L-ácido láctico) em diferentes condições de temperatura e concentração de catalisador, utilizando nitrogênio gasoso para purgar o reator, comparando os perfis de conversão resultantes e as massas molares médias finais. Os resultados demonstraram que um longo período de indução ocorreu quando o nitrogênio gasoso não foi utilizado. Esses resultados sugerem que o nitrogênio possibilita a remoção efetiva da água do sistema de reação, uma vez que os períodos de indução não foram observados quando o gás foi injetado antes da polimerização. O uso de nitrogênio gasoso evitou o processo de despolimerização evidenciado pela obtenção de massas molares mais elevadas do que aquelas em que a purga não foi realizada.

Palavras-chave: Biopolímeros. Despolimerização. Nitrogênio Gasoso. PLLA. Poli(L-ácido láctico). Polimerização por Abertura de Anel.

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Introduction

The synthesis of poly (L-lactic acid) (PLLA) can be readily accomplished by the ring opening polymerization of L-lactide, the cyclic dimer of lactic acid, and the most important aspects of the reaction mechanism have been widely discussed in the literature (CAROTHERS; DOROUGH; NATTA, 1932; NIEUWENHUIS, 1992; DOI; FUKUNDA, 1994; GARLOTTA, 2001; NARAYANAN; ROYCHOUDHURY; SRIVASTAVA, 2004; PLATEL; HODGSON; WILLIAMS, 2008; TIAN et al., 2011). It was demonstrated that the final polymer properties are very sensitive towards the presence of traces of water so the reaction must be carried out in inert, dry medium. Even atmospheric moisture must be purged from the polymerization vessel in order to avoid the deleterious effect of water since it is a strong chain transfer agent in the L-lactide polymerization and also can lead to side reactions. Moreover, small amounts of water can be responsible for the accelerated polymer hydrolysis which results in the depolymerization phenomenon (NIJENHUIS; GRIJPMAN; PENNING, 1992; HYON; JAMSHIDI; IKADA, 1997; BENDIX, 1998; GROOT et al., 2010).

Water is usually removed from the reaction medium by the freeze-thawing procedure (KASPERCZYK, 1995) or by the application of extreme vacuum (NIJENHUIS; GRIJPMAN; PENNING, 1992). Although the efficiency of both techniques was confirmed they unequivocally lead to the increase in the polymerization procedure complexity. The injection of gaseous nitrogen in the reaction vessel is a promising choice but its feasibility must be evaluated mainly in respect to the polymerization profile. Moreover, attention must be paid to the possibility of induction periods or depolymerization.

The aim of this work was to evaluate the injection of gaseous nitrogen in the polymerization of L-lactide as a purging method to remove traces of water. Gaseous nitrogen was then used in

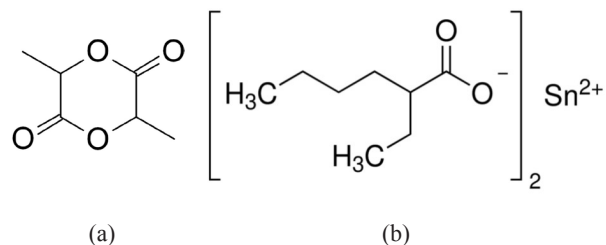
the synthesis of poly(L-lactic acid) at different temperatures and catalyst concentrations and the polymerization profiles and final average molar masses were determined.

Methodology

Materials

The chemical structures of the dimer L-lactide (Purasorb L, Purac) and catalyst tin II 2 ethylhexanoate (Sigma Aldrich) are presented in Figure 1. Gaseous nitrogen (99.9% purity) was injected in the reaction ampoules unless stated otherwise. Methanol, chloroform and tetrahydrofuran were used as solvents. All reactants were used as received without further purification. Acid content of L-lactide before reaction was measured by titulometric analysis yielding a value of 5.6 M_{eq}/g .

Figure 1 - Chemical structure of (a) L-lactide and (b) tin II 2 ethylhexanoate.



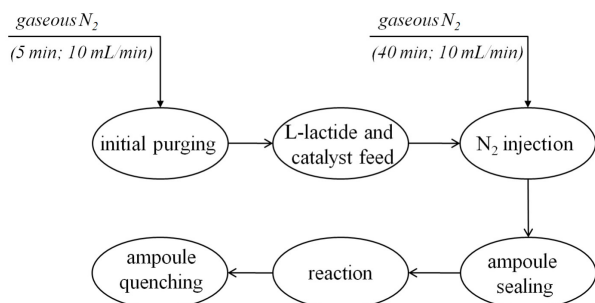
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Polymerization procedure

L-lactide ring opening polymerization was carried out as described by Nijenhuis, Grijpman and Pennings (1992) and Hyon, Jamshidi and Ikada (1997) with some modifications (Figure 2). First, 10 mL glass ampoules were purged with gaseous nitrogen for 5 minutes at 10 mL/min. L-lactide and catalyst were added in the ampoules and then gaseous nitrogen was fed for 40 minutes when

indicated. The ampoules were kept at atmospheric pressure then sealed and heated in an oil bath at 120°C or 140°C for 2, 4, 6, 20, 22 and 24 hours. After the removal from the oil bath the ampoules were immediately quenched in cold methanol (10°C) in order to halt polymerization since at this temperature polymer and L-lactide were solid and polymerization rates were negligible due to the glass effect (MARTEN; HAMIELEC, 1982; TEFERA; WEICKERT; WESTERTERP, 1997). The L-lactide/catalyst molar ratios used were 5,000 and 11,000 $\text{mol}_{\text{L-lactide}}/\text{mol}_{\text{catalyst}}$ as suggested by Hyon, Jamshidi and Ikada (1997).

Figure 2 - Polimerization procedure.



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Characterization

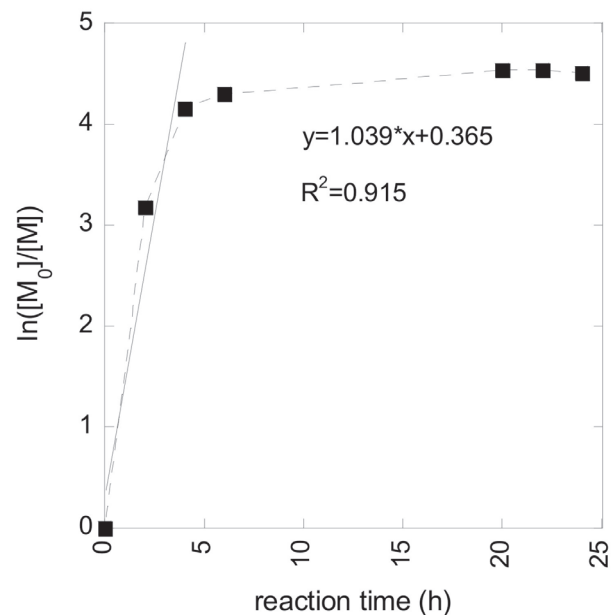
L-lactide conversion was determined gravimetrically. Ampoules were broken and the poly(L-lactic acid) was dissolved in chloroform for 2 hours at 60 rpm. After, the polymer was precipitated in cold methanol and dried at 40°C in a circulating oven until constant weight. Average molar masses were determined by Gel Permeation Chromatography (GPC) using tetrahydrofuran as eluent at 1 mL/min and a refraction index detector. Calibration curve was obtained using polystyrene standards from 580 to 3,800,000 g/mol (GONÇALVES et al., 2009).

Results and discussion

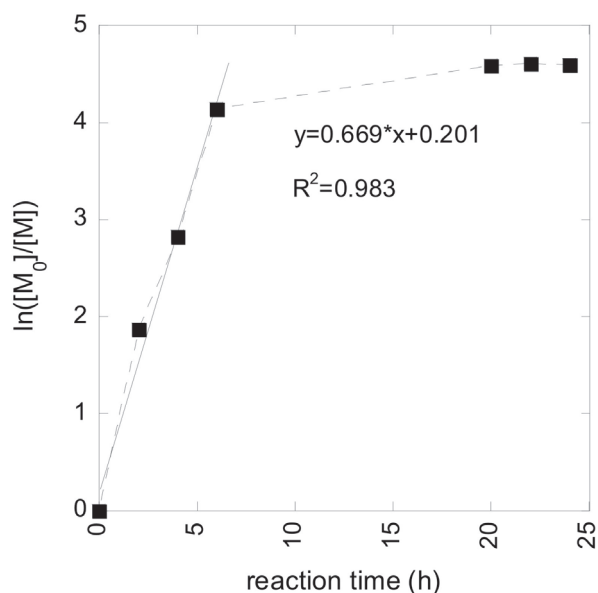
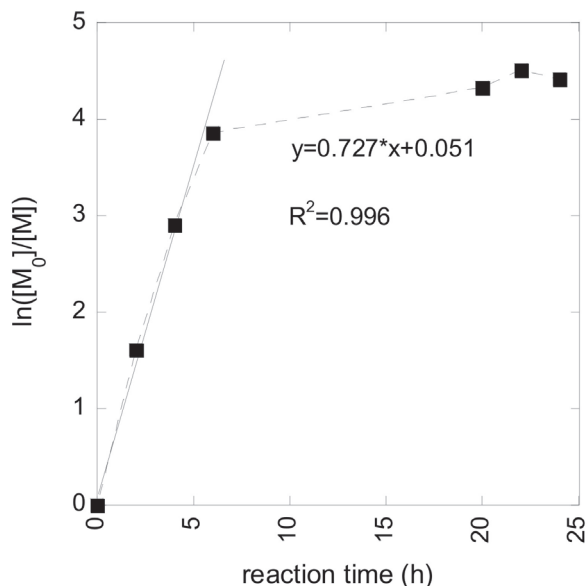
Apparent polymerization rate constants

Figure 3 presents logarithmic L-lactide conversion as $\ln([M_0]/[M])$ versus time for the polymerization at 140°C and catalyst concentrations of 5,000 and 11,000 $\text{mol}_{\text{L-lactide}}/\text{mol}_{\text{catalyst}}$ ($[M_0]$ is the initial L-lactide concentration and $[M]$ is the L lactide concentration at time t). Logarithmic conversion was used in order to linearize the data and also to compare the values found to those presented by Nijenhuis, Grijpma and Pennings (1992). The slope of the initial straight line equals the apparent polymerization rate constant. Gaseous nitrogen was injected in each ampoule for 40 minutes at 10 mL/min. The apparent polymerization rate constants are presented in Table 1 for different experimental conditions.

Figure 3 - Logarithmic conversion ($\ln([M_0]/[M])$) at different catalyst concentration and reaction temperatures (40 minutes of gaseous nitrogen at 10mL/min in all experiments).



(a) 5,000 $\text{mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$ at 140°C.

(b) 11,000 mol_{L-lactide}/mol_{cat} at 140°C.(c) 5,000 mol_{L-lactide}/mol_{cat} at 120°C.

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Table 1 - Apparent polymerization rate constants (k_{app}).

[catalyst] (mol _{L-lactide} /mol _{cat})	Temperature (°C)	Gaseous nitrogen*	k_{app} (s ⁻¹)
5,000	140	Yes	10.4x10 ⁻⁵
11,000	140	Yes	7.3x10 ⁻⁵
5,000	120	Yes	6.7x10 ⁻⁵
5,000	120	No	-**

* INJECTED IN THE REACTION AMPOULE FOR 40 MINUTES AT 10ML/MIN.

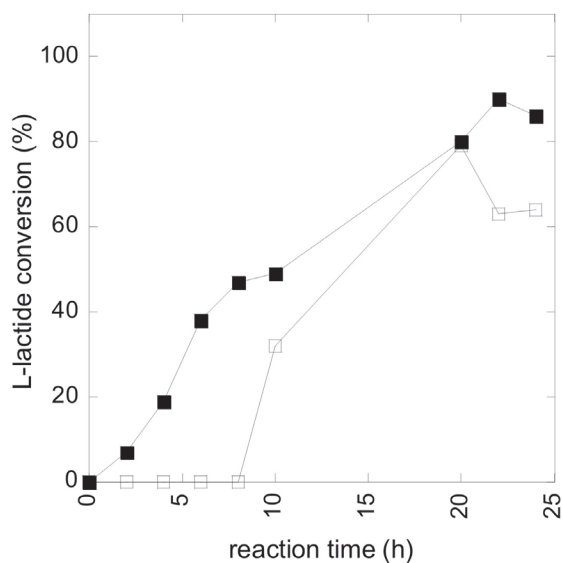
** NOT DETERMINED.

As observed in Figure 3, the relation between $\ln([M]_0/[M])$ and time at the beginning of the reaction is approximately linear indicating that a first order kinetic reaction in respect to the L-lactide concentration can be assumed. Nijenhuis, Grijpma and Pennings (1992) also observed that the first stages of the polymerization followed a first order kinetics and at the later stages the reaction became diffusion controlled. The authors found a value of $15.3 \times 10^{-5} \text{ s}^{-1}$ when the reaction temperature was 110°C and catalyst concentration was approximately 11,000 mol_{L-lactide}/mol_{cat}. One should expect a higher apparent polymerization rate constant at 140°C since higher temperatures lead to higher polymerization rates (HYON; JAMSHIDI; IKADA, 1997). The low rate constant found was probably due to the high acid content of the L-lactide used in this work (5.6 Meq/g) which means that L-lactide was partially degraded and thus could not participate in the reaction (NIJENHUIS; GRIJPMA; PENNING, 1992). Moreover, polymerization rates are dramatically decreased by the presence of free carboxylic groups because they act as chain transfer agents (FORD, 1993; O'BRIEN; CARIELLO; WELLS, 1996). It is worth noting that all experiments were carried out using the same L-lactide meaning that the high acid content did not invalidate the comparisons.

Figure 4 presents the comparison between the conversion profiles obtained with and without gaseous nitrogen injection. In Figure 5 L-lactide

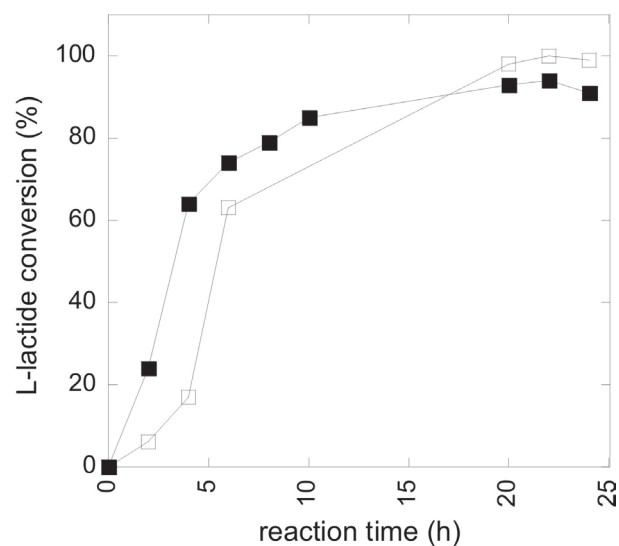
polymerization profiles when 5,000 and 11,000 $\text{mol}_{\text{L-lactide}}/\text{mol}_{\text{catalyst}}$ were used at 140°C and gaseous nitrogen was injected for 40 minutes at $10\text{mL}/\text{min}$ are presented. Figure 6 presents L-lactide polymerization profiles for the reaction temperatures of 120°C and 140°C (catalyst concentrations of $5,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{catalyst}}$) and gaseous nitrogen was injected in the reaction ampoules for 40 minutes.

Figure 4 - L-lactide conversion to PLLA (■) with gaseous nitrogen and (□) without gaseous nitrogen ($5,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$ and 120°C in all experiments).



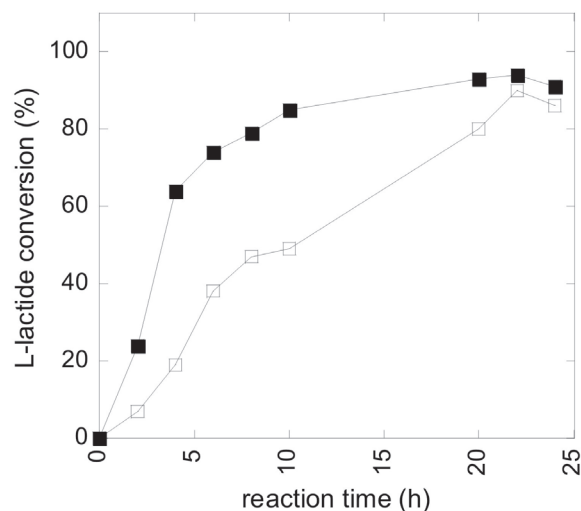
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Figure 5 - L lactide conversion to poly (L-lactic acid) for (■) $5,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$ and (□) $11,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$ (40 minutes gaseous nitrogen at $10\text{mL}/\text{min}$ and 140°C in all experiments).



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Figure 6 - L lactide conversion to poly (L-lactic acid) at (■) 140°C and (□) 120°C ($5,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$, 40 minutes gaseous nitrogen at $10\text{mL}/\text{min}$ in all experiments).



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L-lactide polymerization was faster when a higher catalyst concentration was used as expected. Witzke (1996) proposed a model for conversion as a function of time where the propagation constant (K_p) is a modified Arrhenius equation meaning that the higher the temperature the higher the polymerization rate. Depolymerization at approximately 24 hours was more pronounced when gaseous nitrogen was not injected in the reaction medium. Depolymerization was avoided when a lower catalyst concentration ($11,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$) and 140°C was used together with gaseous nitrogen. This behavior can be attributed to the presence of adsorbed water in both L-lactide and the catalyst that leads to the ester bond breakage and a decrease in the polymer content (HYON; JAMSHIDI; IKADA, 1997; LIM; AURAS; RUBINO, 2008; JAMSHIDI; HYON; IKADA, 1988). This suggests that adsorbed water was efficiently removed from the reaction medium by the use of gaseous nitrogen.

When no gaseous nitrogen was injected in the reaction ampoules a remarkable induction period of approximately 8 hours was observed (Figure 4). This can be explained by the presence of residual water adsorbed in the L-lactide that inhibited polymerization (NIJENHUIS; GRIJPMMA; PENNING, 1992; HYON; JAMSHIDI; IKADA, 1997) and it is another indication that the injection of gaseous nitrogen was effective in removing the traces of water from the reaction system. Due to the inhibition phenomenon the apparent polymerization rate constant was not determined.

Table 2 presents the number average molar mass (MW_n) and weight average molar mass (MW_w) of the final polymer obtained with and without gaseous nitrogen injection. Reactions were carried out at 120°C or 140°C and $5,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$ for 24 hours.

Table 2 - Molar masses of the poly(L lactic acid) obtained with and without the injection of gaseous nitrogen ($5,000 \text{ mol}_{\text{L-lactide}}/\text{mol}_{\text{cat}}$; 24 hours reaction).

Temperature ($^\circ\text{C}$)	Gaseous nitrogen*	MW_n (g/mol)	MW_w (g/mol)
140	Yes	32,000	48,000
140	No	18,000	32,400
120	Yes	40,000	64,000
120	No	21,000	33,600

*INJECTED IN THE REACTION AMPOULE FOR 40 MINUTES AT $10 \text{ mL}/\text{MIN}$.

The influence of temperature was in accordance with the literature since a low reaction temperature led to a higher average molar mass (BENDIX, 1998). Experimental sets where nitrogen was not injected in the reaction system presented lower average molar masses than the cases where the ampoules were purged with gaseous nitrogen. This is in accordance with the fact that the presence of traces of water when no nitrogen was used led to an increased depolymerization of the poly(L-lactic acid) chains as shown in Figure 4, resulting in a lower average molar mass of the final polymer (NIJENHUIS; GRIJPMMA; PENNING, 1992; HYON; JAMSHIDI; IKADA, 1997; MOTTA; DUEK, 2006).

Conclusions

Gaseous nitrogen injection was investigated in order to remove traces of water that could affect the L-lactide ring opening polymerization. Reactions carried out with and without the injection of gaseous nitrogen in the reaction ampoules showed that the nitrogen injection had remarkable effect on the polymerization profiles since an induction period of 8 hours was observed when no nitrogen was used. Average molar masses of the final polymer were lower when no nitrogen was used due to an enhanced depolymerization mechanism caused by traces of water adsorbed on L-lactide. Results suggest that the injection of gaseous nitrogen is an effective, low cost way to prevent the influence of water on the polymerization of L-lactide.

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