

Study on the Viability in Replacement of Metallic Catalysts by Enzymatic in the Polymerization Reaction of Poly(Lactic Acid).

Aruã C. da Silva¹ (PG), **Leandro H. de Andrade**¹ (PQ), **Susana I. C. de Torresi**¹ (PQ)*. Email: aruacs@iq.usp.br

¹Universidade de São Paulo, Instituto de Química, Av. Prof. Lineu Prestes 748, Cidade Universitária, 05513-970, São Paulo, SP, Brasil.

Keywords: poly(lactic acid), catalysis enzymatic, immobilized lipases, biomaterials.

Introduction

Poly (lactic acid) (PLA) is a well known polymer by its properties of biodegradability and biocompatibility. Therefore it is very useful in the biomedical field¹. The Sn(Oct)₂ catalyst is widely used for the synthesis of such polymer due to its high efficiency. However, their use in biomedical applications remains questionable² due to the small amount of 2-ethylhexanoic acid remaining from the preparation of the catalyst, which is very toxic³. Furthermore, tin itself presents considerable toxicity⁴.

An alternative for the replacement of the metallic catalyst is through the use of enzymatic catalysis, using lipases that catalyze ring-opening polymerization of lactides¹.

In this context, the present work aims to show the efficiency of heterogeneous enzymatic catalysis in obtaining PLA instead of metallic catalyst, in order to improve and facilitate the process of obtaining this biomaterial.

Results and Discussions

The preparation of the polymer PLA is carried out in a one-pot reaction by adding the lactide, catalyst and dry toluene. The reaction was refluxed for 24 hours at 110°C using Sn(Oct)₂, while by enzymatic route was tested at 30, 50 and 80°C, in order to soften the conditions for reuse the immobilized enzymes. Furthermore, two different immobilized lipases were tested, named CAL-B (Sigma Aldrich) and PSC II (Sigma Aldrich).

Figure 1 shows a simplified scheme of the polymerization reaction for synthesize the PLA.

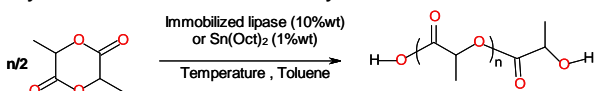


Figure 1. Ring-opening and polymerization of PLA.

In order to make a comparison between the properties of the polymer obtained by metallic catalyst and via enzymatic, the products were subjected to MALDI-TOF and analyzed by PolyTools1.2 software to obtain parameters such as repetition unit, number average molecular weight

(Mn), weight average molecular weight (Mw) and polydispersity, as shown in **Table 1**.

Table 1. Parameters obtained from MALDI-TOF.

	Rep. Unit (Da)	Mn (Da)	Mw (Da)	Polydispersity
Mettalic Catalyst (SnOct ₂)	72.0245	2045.74	2157.27	1.0546
Enzymatic Catalyst (PSC II 80°C)	72.0197	2323.25	2512.53	1.0812
Enzymatic Catalyst (CAL-B 80°C)	72.0197	2262.79	2429.92	1.0739

It can be seen that the polymer obtained enzymatically presents polydispersity and chain size similar to that obtained classically by metal catalyst.

Conclusions

Through the presented results, it is concluded that it is possible to replace the metal catalyst for the enzyme, since the lipases studied performed the polymerization reaction and it results in a polymer presenting the desired chain length.

Acknowledgment

The authors are thankful to FAPESP (14/09353-6) for financial support in the project and the granted scholarships.

¹Fujioka, M.; Hosoda, N.; Nishiyama, S.; Noguchi, H.; Shoji, A. SEN'I GAKKAISHI 2006, 62, 63–65.

²Schwach, G.; Coudane, J.; Engel, R.; Vert, M. Journal of Polymer Science Part A: Polymer Chemistry 1997, 35, 3431–3440.

³Juberg, D. R.; David, R. M.; Katz, G. V.; Bernard, L. G.; Gordon, D. R.; Vlaovic, M. S.; Topping, D. C. Food and Chemical Toxicology 1998, 36, 429–436.

⁴Winship, K.A. Adverse Drug React Acute Poisoning Rev. 1988, 7, 1, 19-38.