XIV Congreso Nacional de Biotecnología y Bioingeniería

ONE-POT BIOCATALYTIC SYNTHESIS OF SUGAR BASED POLY (ε-CAPROLACTONE)

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Palabras clave: biocatalysis, lipase, isosorbide.

Introduction. The ability to attach synthetic polymers onto carbohydrates is a pathway to new applications in the fields of detergents, packaging, and pharmaceuticals. In the case of some aliphatic polyesters, this approach leads to an increment in the biodegradability of the target polymers. Water soluble and dispersible polymers are in great demand for applications as detergents and surfactants. Low molecular weight amphiphilic compounds such as fatty acid esters of carbohydrates also function as useful surfactants. However, selective functionalization of carbohydrates is difficult to achieve, as carbohydrates contain multiple hydroxyl groups with different chemical reactivity. Selective monoacylation of the carbohydrate is only obtained using protective group strategies. Deprotection steps are required and the synthetic scheme becomes complicated. Enzymes are highly selective catalysts and therefore they have been used to regioselectively acylate carbohydrates. Lipase-catalyzed polyester synthesis is an attractive alternative to poorly selective chemical catalysts [1].

In this work, studies on the bulk ring-opening polymerization of ε-caprolactone induced by immobilized *Yarrowia lipolytica* lipase (YLL) in the presence of isosorbide is reported. Products were characterized by ^{1}H and ^{13}C- NMR, MALDI-TOF and DSC.

Polyester synthesis

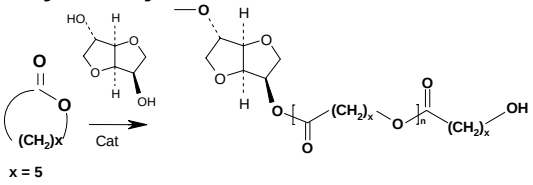

Fig. 1 *Yarrowia lipolytica* catalyzed polymerization of ε-caprolactone and isosorbide to form biodegradable amphiphilic polyesters [2].

Structural analyses were made by MALDI-TOF, ^{1}H, and ^{13}C-NMR.

Results and Discussion.

Experiments were performed to determine the reaction order of monomer. The effect of incubation times, isosorbide concentration, resin type and temperature in the polymerization of ε-CL were evaluated. Figure 2 shows the kinetic studies in function of time and isosorbide concentration. Lowest conversions of ε-CL to PCL-isosorbide were observed when lipase was immobilized on Lewatit TP214 at 70 ºC and 0.5 mmol of isosorbide. One of the reasons of this behavior is the distribution of the enzyme into the polymeric resin, which is affecting the specificity of the enzyme. It was observed that higher conversions were obtained when isosorbide concentration was lower, this can be attributed to the fact that all the active sites of the lipase are in the form of enzyme-activated monomer and enzyme-activated initiator and this converts the reaction rate slower. From the results on YLL activity as a function of particle size and surface area for styrenic and polystyrenic resins, the percent surface area occupied by YLL is a critical factor that can be used to improve immobilized YLL activity. Increased percent accessible surface area will increase the probability of collisions between substrates and YLL. As the matrix active group changes in the styrenic resins, a corresponding increase in polyester synthesis reaction rates was observed.

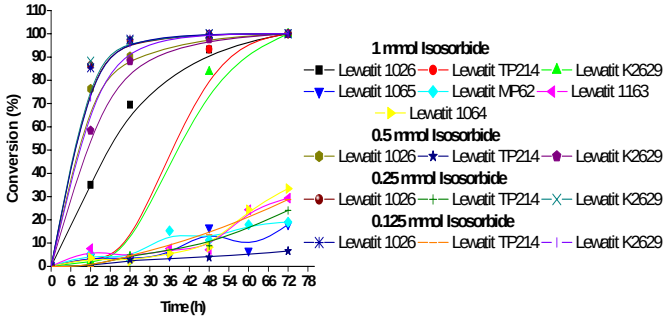

Fig. 2. Monomer conversion as a function of time for the enzyme-catalyzed ε-caprolactone-isosorbide polymerizations at 70 °C. R= 1 mmol ε-CL/12 mg immobilized lipase.

Conclusions. A convenient one-pot biocatalytic synthesis of novel biodegradable amphiphilic oligomers is described. The selectivity of different immobilization matrices and general applicability of the method was also demonstrated by screening a number of commercial matrices with *Yarrowia lipolytica* lipase. Thus, by this strategy, chains were formed having sugar headgroups without using protection-deprotection strategies.

Acknowledgments. Financial support by CONACyT, Grant SEP-2004-C01- 47173E. We acknowledge M.D.J. Ramírez-Quijas for sample preparation. We are indebted to Ángel Marcos-Fernández and Rosa Lebrón-Aguilar (CSIC, Madrid España) for MALDI-TOF spectra.

References

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