ENZYMATIC APPROACH FOR THE SYNTHESIS OF ε-CAPROLACTAM AND HYDROXY ACIDS POLYESTERAMIDES

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Introduction

Over the last years, the trends in polymer synthesis are being characterized by a dynamic development of the enzymatic synthesis pathway, emphasizing in this manner the production of new functional polymeric materials[1]. Considering the continuous development of green processes, there is an increasing interest in polymers synthesis using enzymes as biocatalysts, as the new biobased polymeric products are exhibiting a remarkable diversity, meeting the criteria of sustainability, biodegradability, biocompatibility, and eco-friendliness[2].

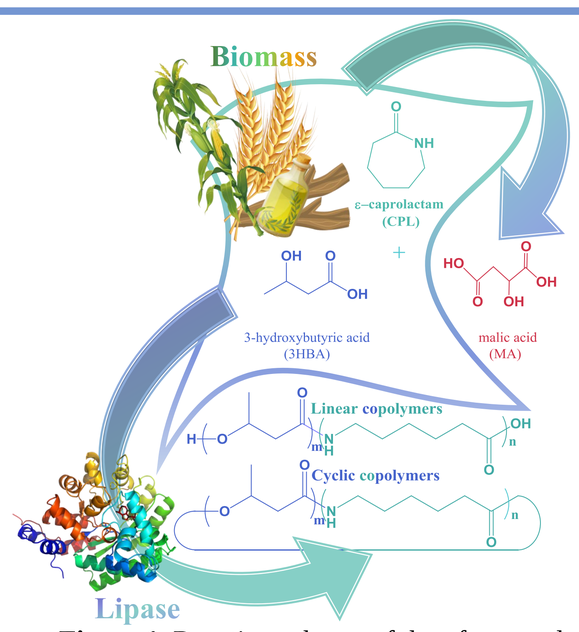

Figure 1. Reaction scheme of the of ε-caprolactam polymerization with biobased hydroxy acids

Aim of the study

Polyesteramides are a group of polymers of increasing importance with several possible applications in the biomedical and pharmaceutical fields[3]. Therefore, in this work, the enzymatic synthesis of novel copolymers of ε-caprolactam with two hydroxy-acids was investigated. The reactions were carried out in solvent-free systems, at temperatures up to 80°C, using Novozyme 435 and GF-CalB-IM biocatalysts. The chemical structure of the reaction products was confirmed by FT-IR and MALDI TOF-MS.

Results and discussions

The effect of monomers molar ratio

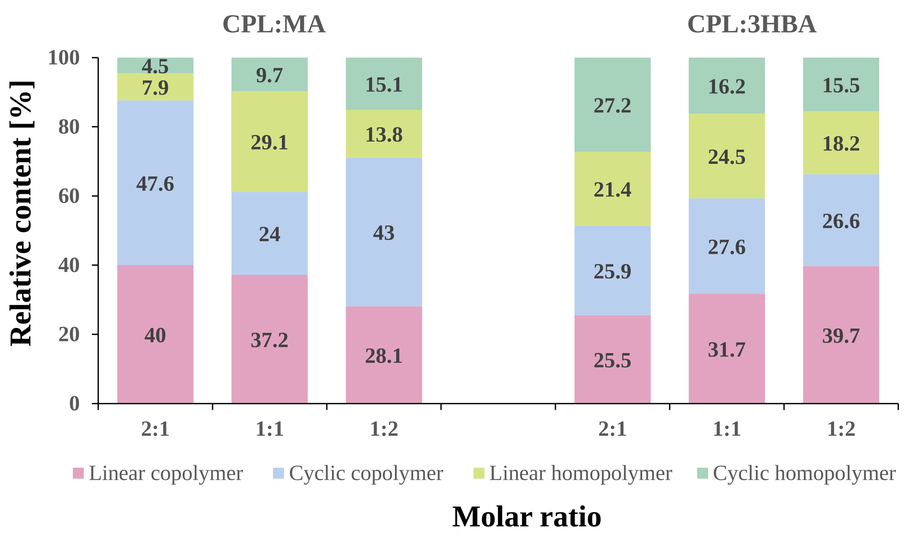

Figure 2. The influence of the molar ratio of monomers on the relative composition of the copolymers synthesized from ε-caprolactam (CPL) with L-malic acid (MA) and 3-hydroxybutyric acid (3HBA)

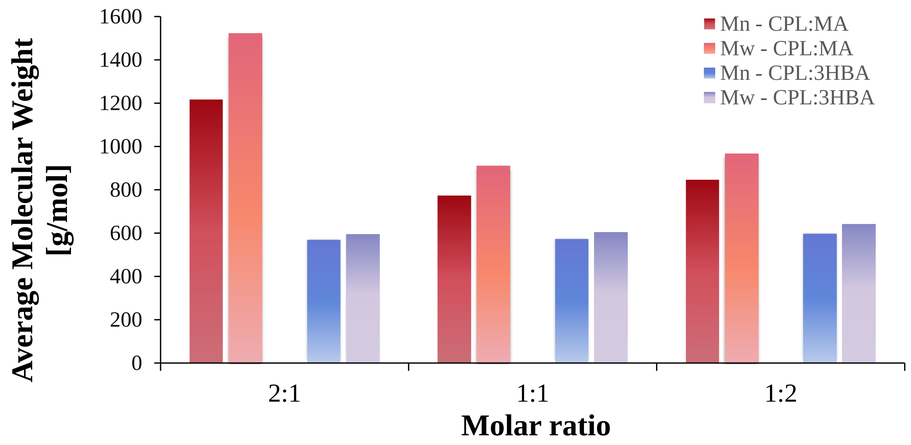

Figure 3. The influence of the molar ratio on the average molecular weights of the copolymers of ε-caprolactam (CPL) with L-malic acid (MA) and 3-hydroxybutyric acid (3HBA)

The influence of the reaction time

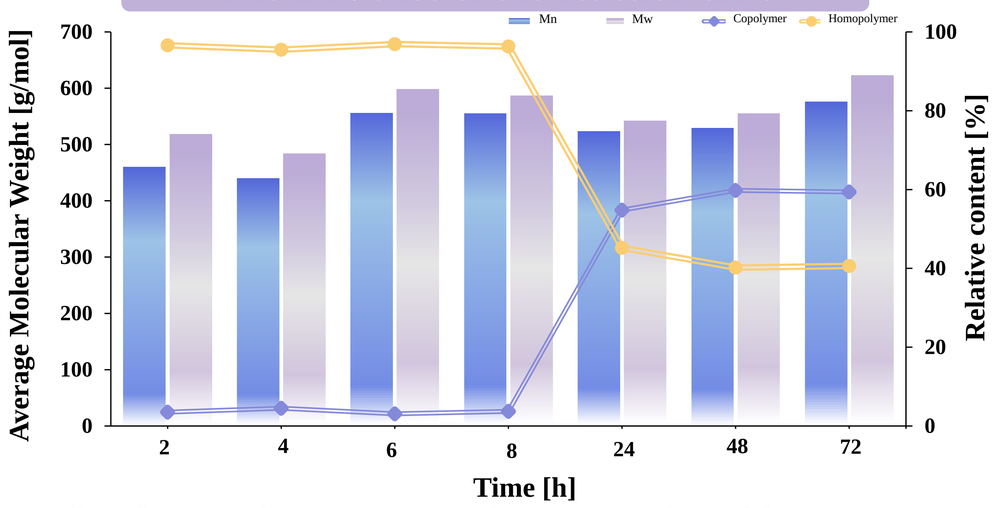

Figure 4. The influence of the reaction time on the reaction products of the ε-caprolactam (CPL) and 3-hydroxybutyric acid (3HBA) catalyzed by Novozyme 435, with CPL:3HBA molar ratio 1:1, in a solvent less system, at 80°C

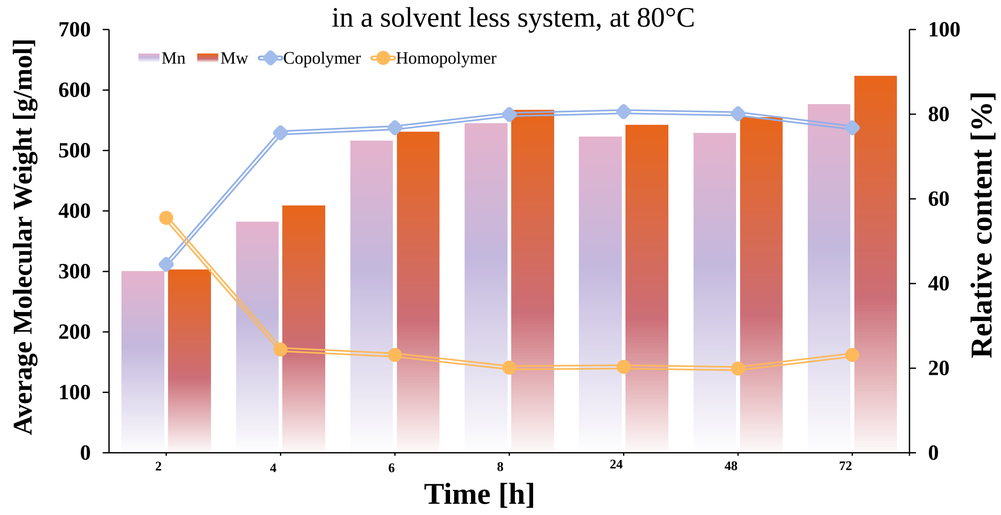

Figure 5. The influence of the reaction time on the reaction products of the ε-caprolactam (CPL) and L-malic acid (MA) catalyzed by Novozyme 435, with CPL:MA molar ratio 1:1, in a solvent less system, at 80°C

Products characterization by FT-IR Spectroscopy

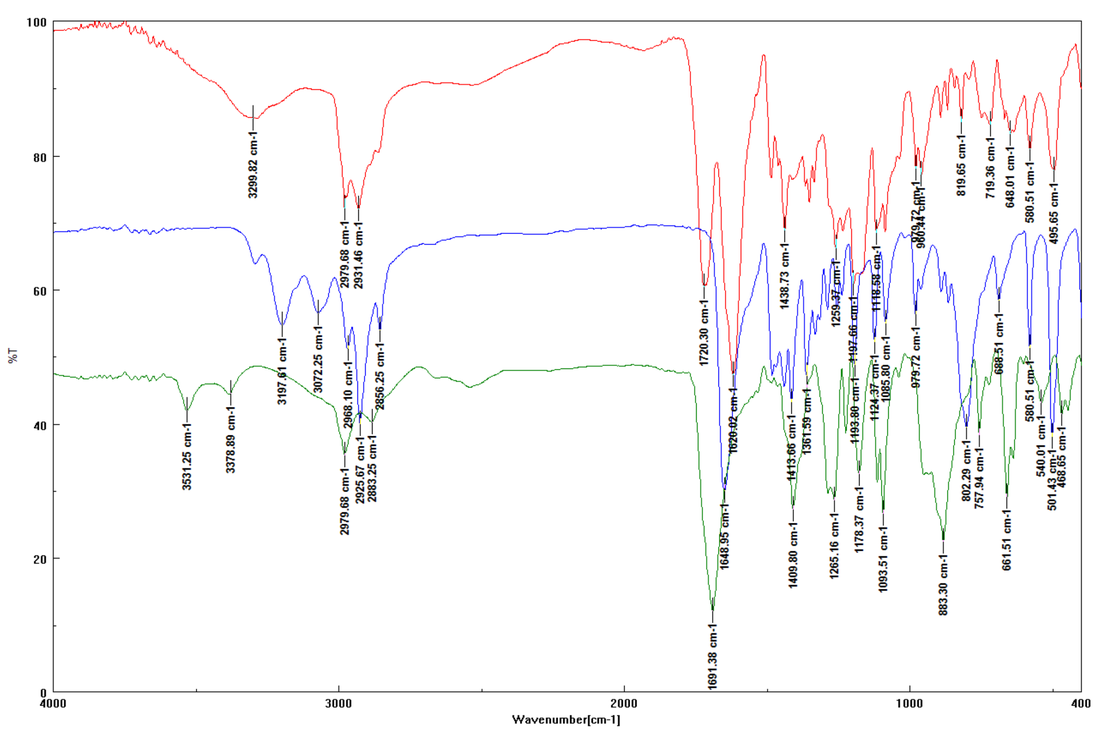

Figure 6. FT-IR spectra of ε-caprolactam and L-malic acid copolymer (red), ε-caprolactam (blue) and L-malic acid (green)

Products characterization by MALDI TOF-MS spectrum

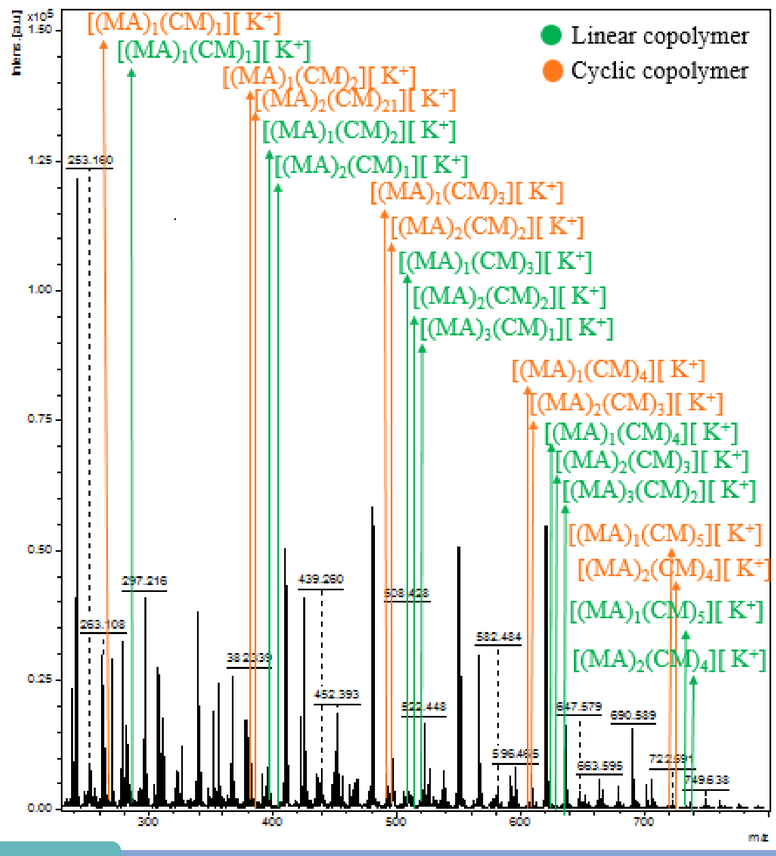

Figure 7. Structure confirmation of the ε-caprolactam (CPL) and L-malic acid (MA) reaction products by MALDI TOF-MS spectrum , synthesized with Novozyme 435, at 1:1 CPL:MA molar ratio and 80°C, in solvent less system

Conclusions

- The present study achieved the synthesis of two new polyesteramides of ε-caprolactam (CPL) with L-malic acid (MA) and 3-hydroxybutyric acid (3HBA) using the enzymatic biocatalytic pathway.
- The formation of copolymers with higher medium molecular mass was enhanced at a molar ration of 2:1 ε-caprolactam to hydroxy acid and by a longer reaction time, up to 72 hours.
- The synthesis of novel polyesteramides is driving the evolution of new biopolymers, creating a more favorable landscape in the biobased and biodegradable polymer market.

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