Biocatalytic degradation of poly(lactic acid) to monomers using a chemically modified lipase in ionic liquids

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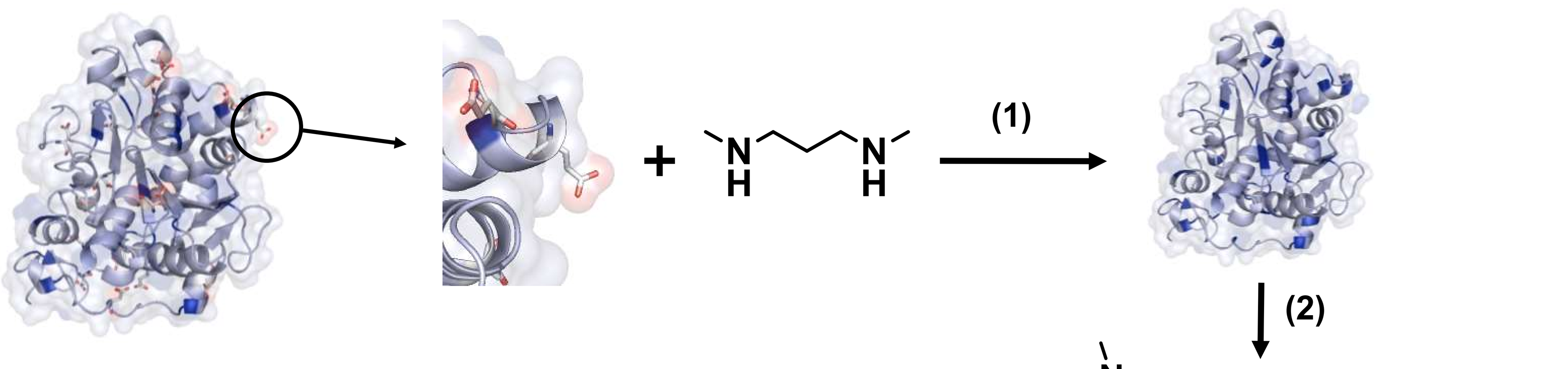
Introduction

Biocatalytic degradation of plastics is a highly attractive alternative to chemical degradation. However, the thermostability and activity of enzymes is typically below the glass transition of plastics making unsuitable for this process.

Brogan *et al.* have previously demonstrated that proteins can be **chemically modified** to form biofluids with an improved **thermal stability** and **enzymatic activity** in different ionic liquids.[1-4] **Ionic liquids**, organic salts with melting temperatures below 100 °C, are promising **non-aqueous solvents** for industrial processes due to the highly tuneable nature of their attractive solvent properties.

Here, we demonstrate the chemoenzymatic depolymerisation of post-consumer **poly(lactic acid)** through facile modification of Lipase B from *Candida antarctica*, **CalB**, and using **ionic liquids.**[4]

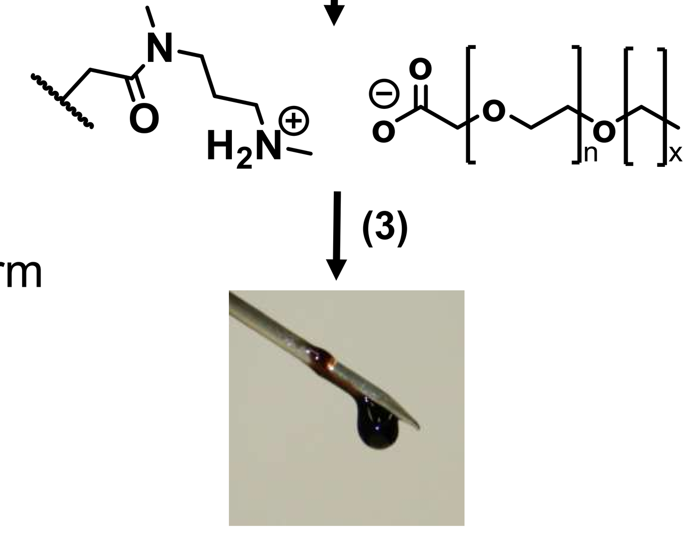
Enzyme modification



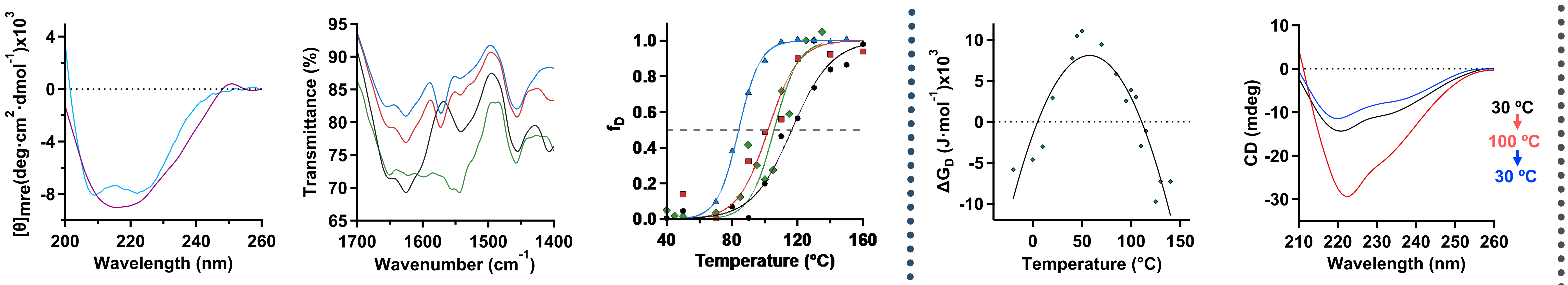
(1) **Cationization** of surface carboxylic acid residues (Asp and Glu) of CalB.

(2) **Electrostatic coupling** of polymer surfactant to form the nanoconjugated CalB, [C-CalB][S].

(3) **Lyophilisation** and **annealing** of nanoconjugated CalB to yield **solvent-free liquid protein**.



Stability of modified lipase in ionic liquids

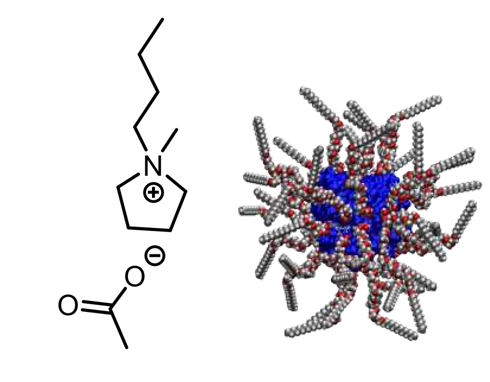


High conservation of secondary structure (SCRD) in the absence of water.

Secondary structure is retained in ionic liquids as predominately α-helix (FTIR).

Higher thermostability in anhydrous conditions (T_m > 80 °C) than in water (T_m = 71 °C)

Key: Aqueous; Solvent-free biofluid; [bmpyrr][OAc]; [bmpyrr][$MeSO_4$]; [bmpyrr][OTf]; [bmpyrr][NTf_2]

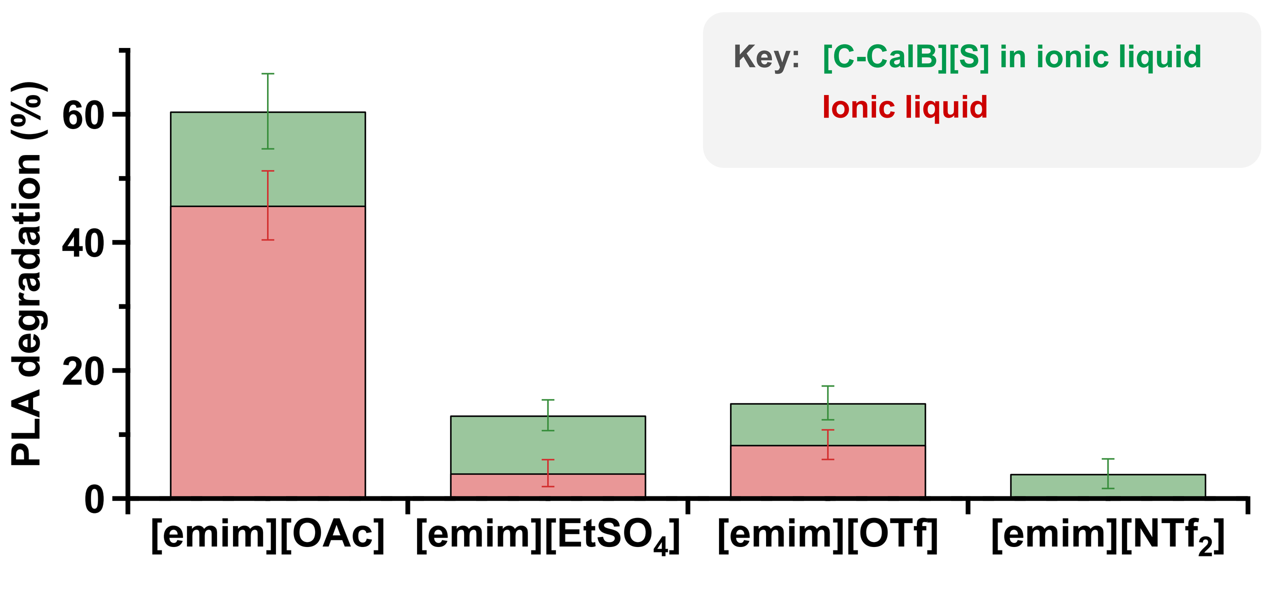


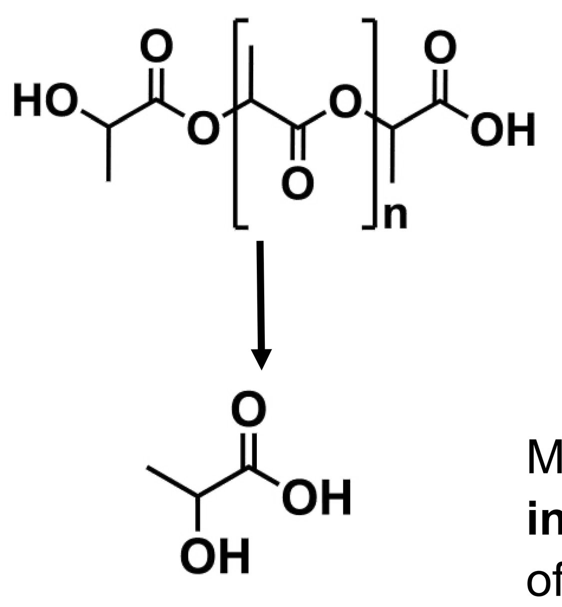
Modified CalB in [emim][OAc] forms:

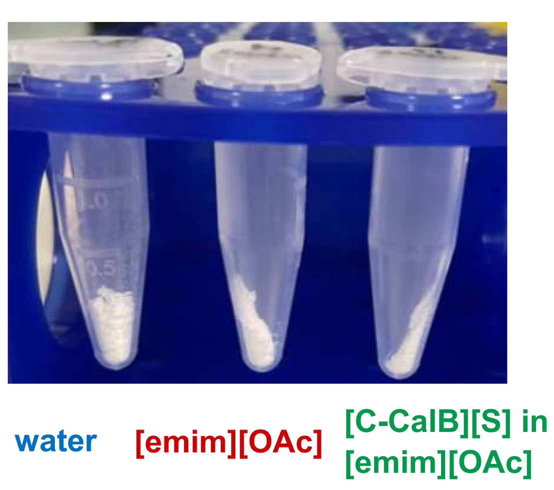
- A **thermophilic material** with high stability between 20 and 120 °C.
- A **dynamic material** able to almost fully recover its structure after heating.

Modified lipase in [emim][OAc] for the degradation of PLA

PLA powder degradation at 60 °C for 20h

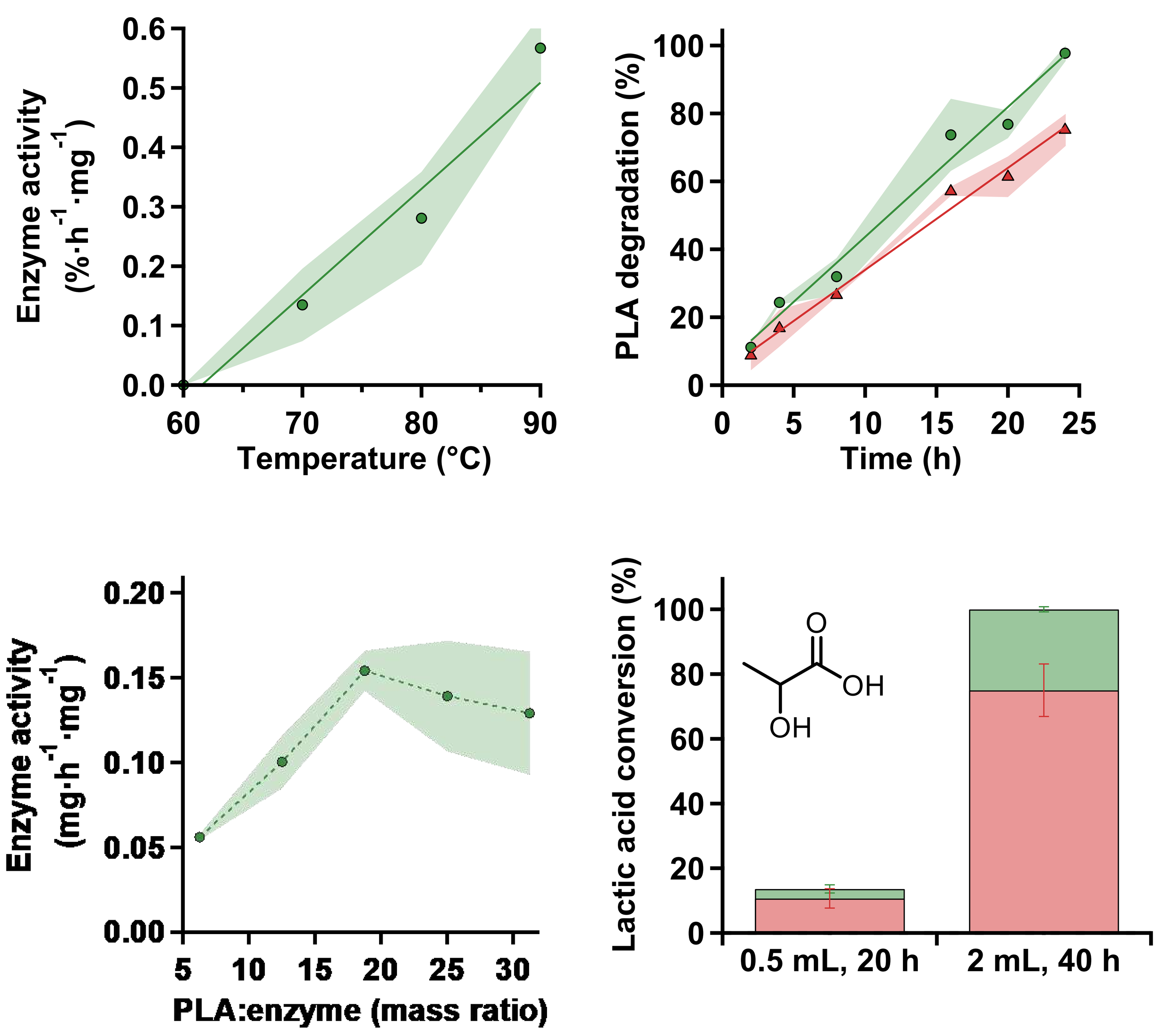


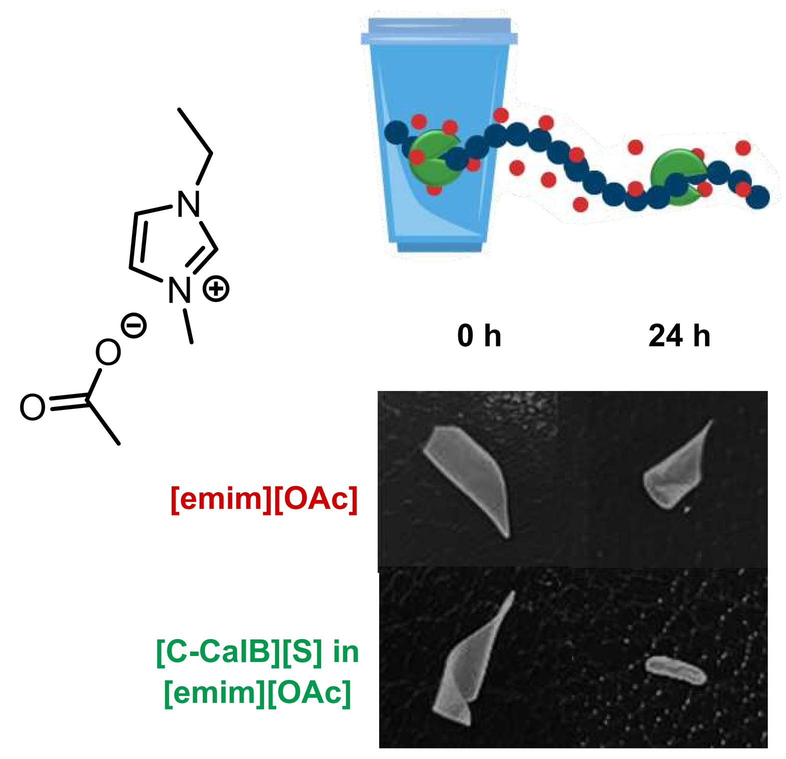




Modified CalB in [emim][OAc] **increases 13%** the degradation of PLA powder.

Post-consumer PLA plastic degradation





Activity of the modified CalB for the degradation of PLA plastic in [emim][OAc]:

- Activity **increases with increasing temperature**.
- **zero-order kinetics** - modified CalB is not inhibited.
- The **maximum activity** of modified CalB is 0.15 $mg{\cdot}h^{-1}{\cdot}mg^{-1}$.
- Modified CalB improves **lactic acid production.**

Conclusion

CalB was successfully stabilised by chemical modifications, showing a preservation of its secondary structure in anhydrous conditions with a high α-helix content, and a high thermal stability in ionic liquids. Furthermore, modified CalB in [emim][OAc] was able to completely degrade post-consumer PLA plastics at 90 °C and fully convert PLA to monomer.

As a result, we showed that chemical modification can improve protein stability. Moreover, through combining modified enzymes and ionic liquids, we can improve their enzymatic activity to degrade plastic polymers.

References

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