Low Temperature Lipase-Catalysed Synthesis of Renewable Functional Telechelics in $scCO_2$

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Introduction

Natural resources can be exploited to extract from them the **monomer** materials required to prepare novel **renewable polymers** [1]. Also, **supercritical CO_2 ($scCO_2$)** has been the focus of much research as a **green reaction medium** for polymerisations [2].

- We have investigated the **plasticising effects** of $scCO_2$ on a commercially available **semi-crystalline polyester** (*i.e.* poly(ε-caprolactone)) (**Fig. 1**) [3];
- Used this learning to design a green **enzymatic low temperature approach** to prepare **green functional polyesters** (**Fig. 2**) [4];
- The monomer we have focussed upon is the diacid **azelaic acid (AzAc)**, which is normally polymerised at T>200 °C due to its **high melting point** and **insolubility** in apolar solvents.

CO_2-induced plasticisation

The CO_2 molecules interact with the carbonyl groups of **poly(ε-caprolactone) (PCL)**, swelling its structure. This results in a **dramatic decrease** in the **melting point** (T_m) and **viscosity** (η) of the polymer (**Fig. 1**) [3].
This can significantly **ease the synthesis and/or processing** steps by increasing the mobility of the monomers and polymer chains.

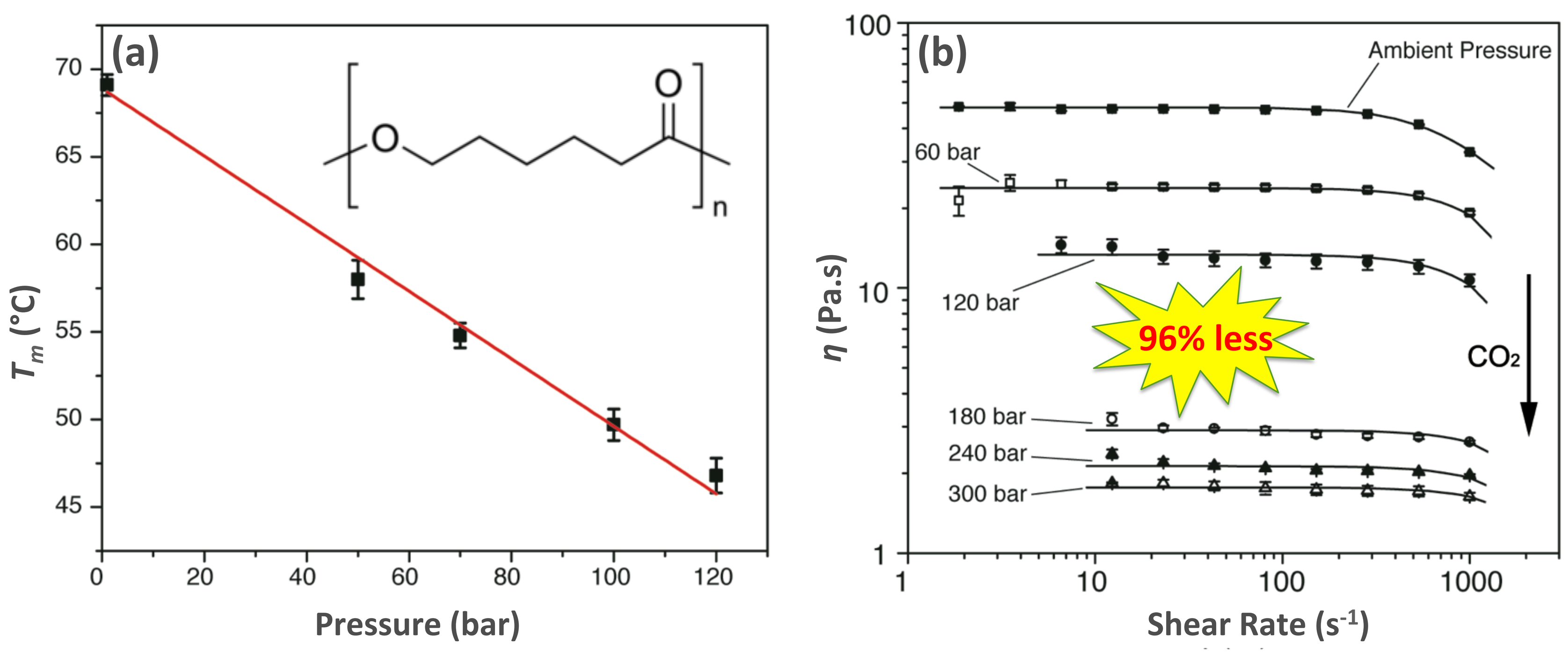

Fig. 1 – Effects of CO_2 on the T_m **(a)** and viscosity **(b)** of PCL (M_n~10 kDa). The polymer structure is shown (inset).

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AzAc can be synthesised from **oleic acid**, or extracted from **barley**, **rye** and **wheat**.

The use of **$scCO_2$ as a reaction medium** for polymerisation with 1,6-hexanediol facilitated the effective use of **Candida Antarctica Lipase B** (**CaLB**) as a catalyst at a temperature as low as **35 °C** (**Fig. 2**) [4].

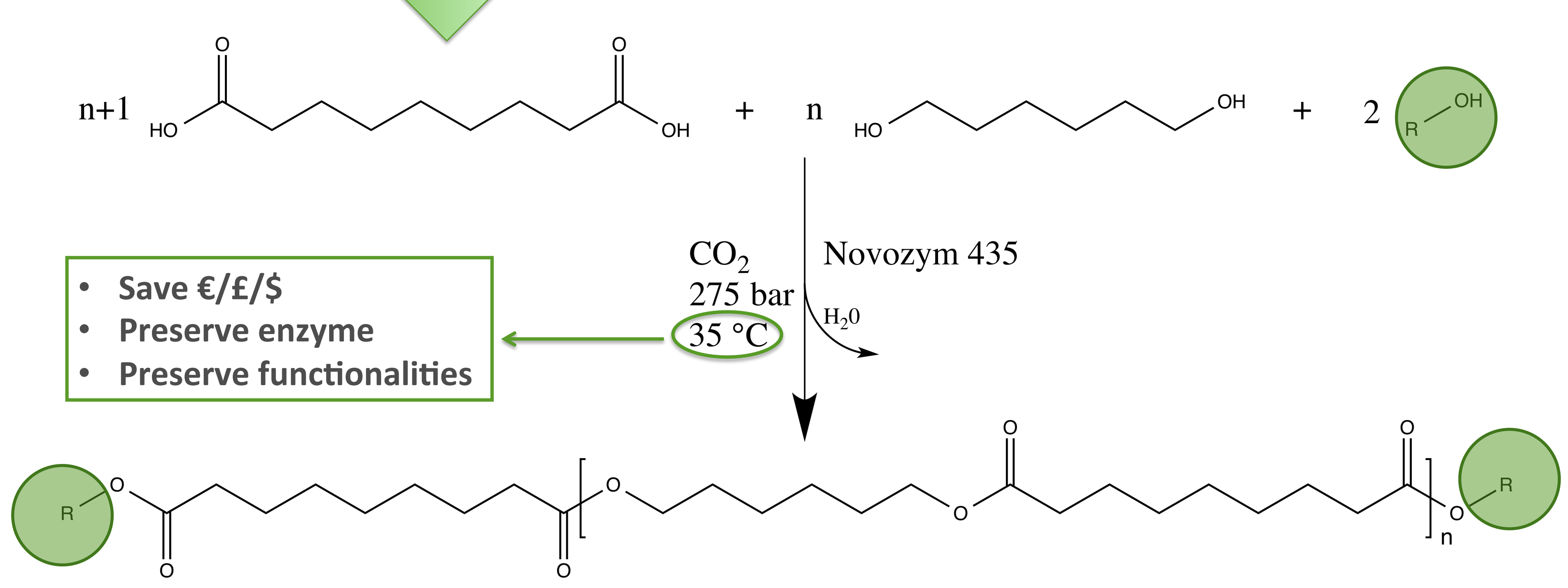

Fig. 2 – Synthesis of functional **poly(hexylene azelate) (PHA)** in $scCO_2$.

The polymer chains were functionalised by using different functional molecules as end-cappers (**Fig. 3**) and characterised by NMR, GPC, DSC and MALDI ToF (**Table 1**).

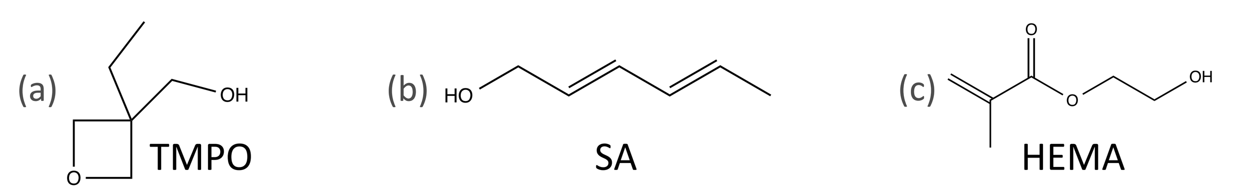

Fig. 3 – End-cappers used in this study: (a) trimethylolpropane oxetane (**TMPO**), (b) sorbic alcohol (**SA**) and (c) 2-hydroxyethyl methacrylate (**HEMA**).

Table 1 – Properties of the functional PHAs synthesised in $scCO_2$.

Product	M_n^{th} (g/mol)	M_n^{NMR} (g/mol)	M_n^{GPC} (g/mol)	Đ	T_m (°C)	Yield (%)	Conversion (%)
PHA-SA	1160	1500	2400	1.96	38.6 ± 0.9	86	98
PHA-TMPO	1196	1100	1500	1.73	29.1 ± 0.2	87	96
PHA-HEMA	1230	1500	1700	2.18	31.0 ± 0.4	78	98

Reaction system

The reactions were carried out in an in-house manufactured **stainless steel-316 batch reactor** equipped with an overhead stirrer (**Fig. 4**).

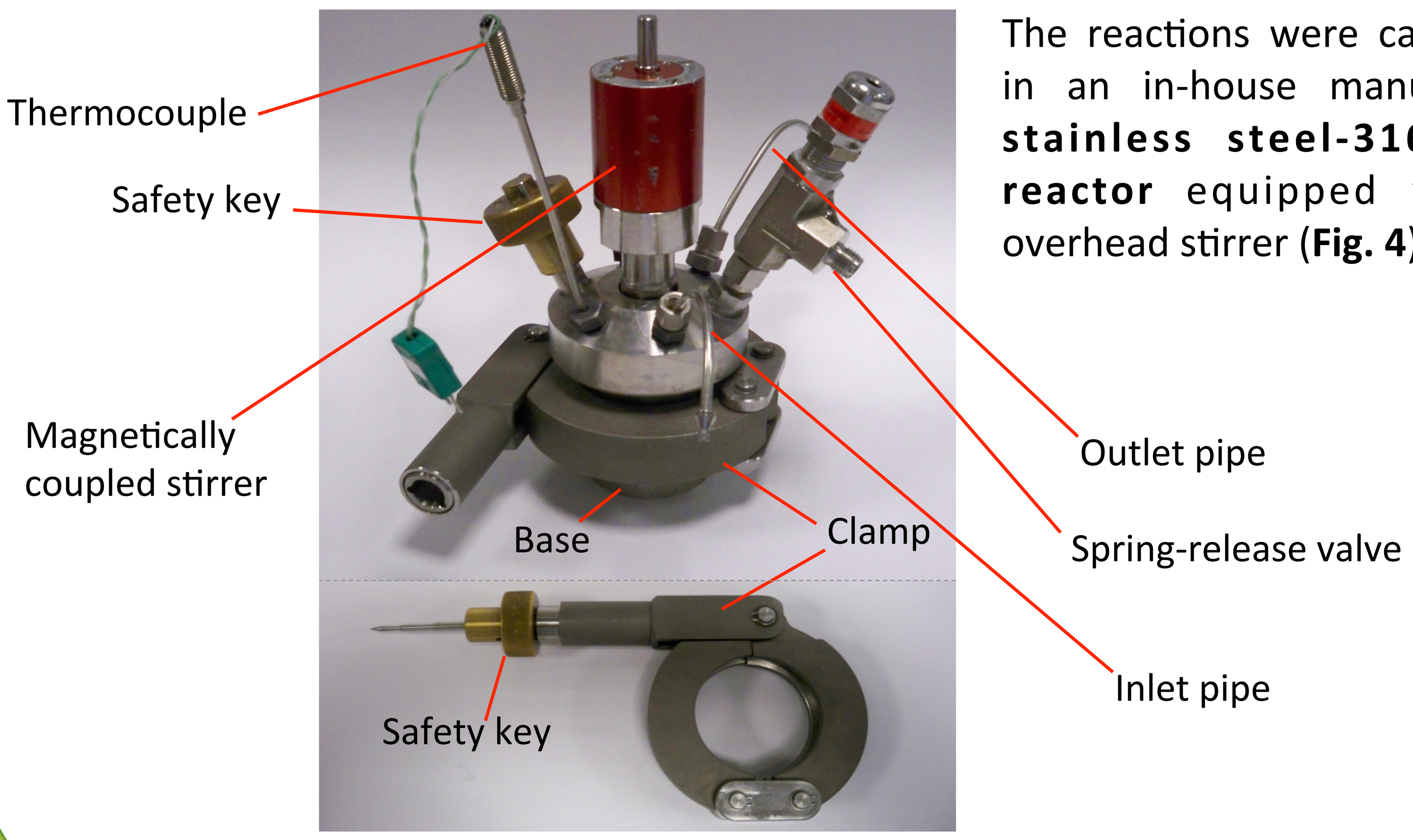

Fig. 4 – Stainless steel clamp-sealed vessel used for the polymerisations.

Enzyme recycling

The **activity of the enzyme** used for **five high-pressure reactions** was compared to the activity of **fresh** Novozym 435 and enzyme beads used for a polymerisation in the **melt at 110 °C,** by monitoring the synthesis of propyl oleate (**Fig. 5**). The activity of the enzyme is not reduced by the $scCO_2$, thus the **high-pressure process** is **commercially viable** and sustainable [4].

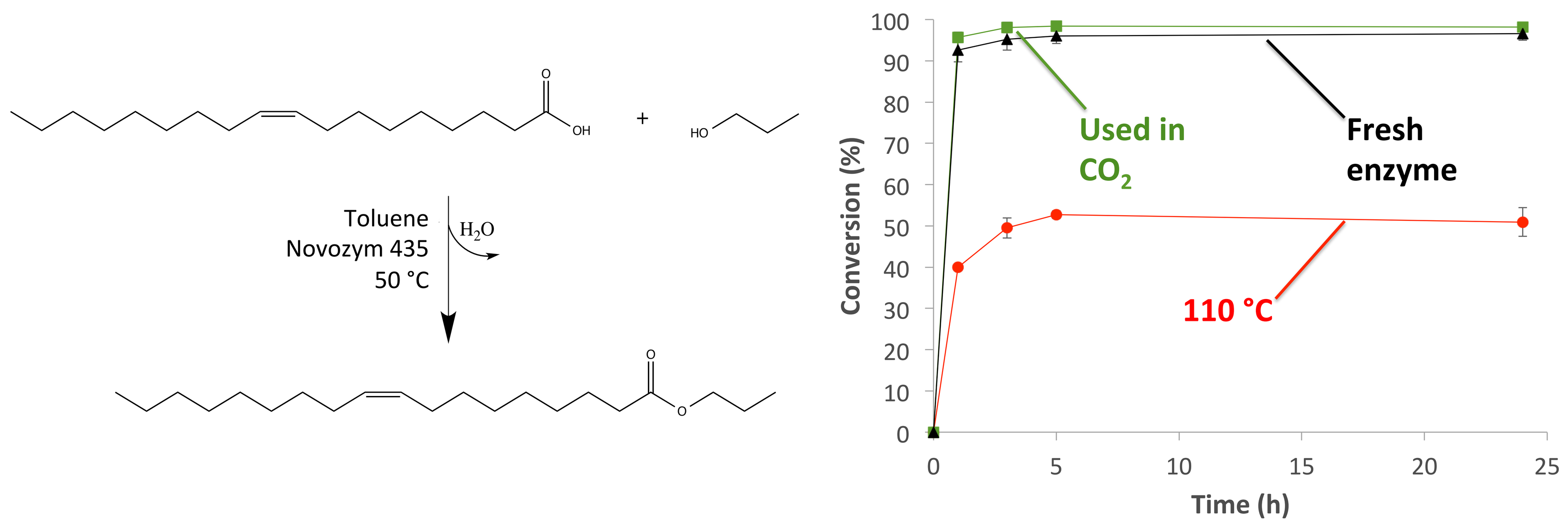

Fig. 5 – Synthesis of propyl oleate (**left**) and reaction conversion (through ^{1}H-NMR, **right**) when using new Novozym 435 and enzyme after: five CO_2 reactions and a reaction in the melt (110 °C)

Conclusions

- The **plasticising effects** of CO_2 have been **assessed on PCL**: significant **reductions** in the **melting point** and **viscosity** were detected
- **Green functional polyesters** have been synthesised in $scCO_2$ through a **new low T approach** with high yields and conversion of the monomers
- **Enzyme recycling** tests showed that high pressure reactions are **commercially viable** and the enzyme can be recycled without activity losses

References

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This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no (289253) .

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