# Solvent-Free Ring Opening Copolymerisation of L-Lactide with a Cyclic Carbonate Derived from D-Mannose and $CO_2$


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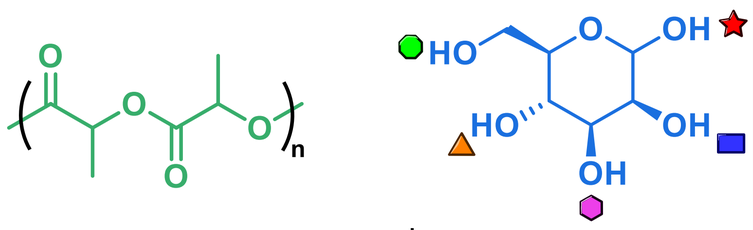
## 1. Background & Aims

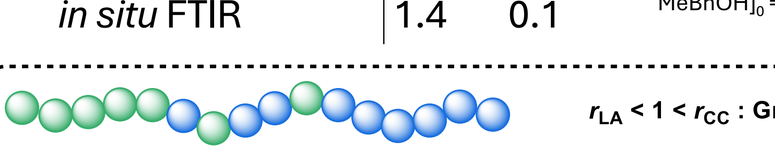
**Poly(lacticacid) (PLA):** + **Sugar feedstock:**

**Leading bioderived polymer**




**Degradable** **Bio-based** **High production** **Commercial** **Thermally processable** [1-4]

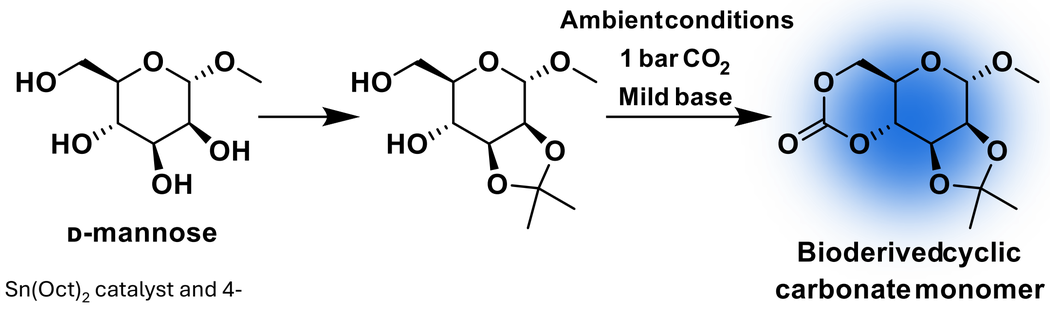
**Cheap** **Abundant** **Functionalisable** [5, 6]



**Desirable properties are incorporated into PLA backbone**

## 2. Synthesis and ROP

- Cyclic carbonate was synthesised from a D-mannose derivative *via* a one-pot carbonation using $CO_2$.[4]



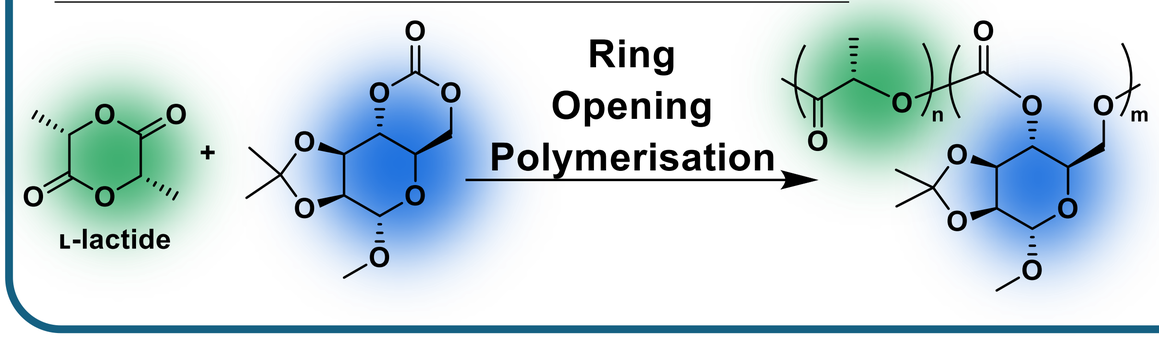

D-mannose

**Bioderived cyclic carbonate monomer**

Table 1: Copolymerisation of **CC** and L-lactide with $Sn(Oct)_2$ catalyst and 4-MeBnOH initiator at 130 °C.

| Entry | $f_{cc}/f_{LLA}$ | Conv. **CC** (%) | Conv. LLA (%) | $F_{cc}/F_{LLA}$ | $M_{n\,SEC}$ [$Đ_M$] (kg mol$^{-1}$) |
|---|---|---|---|---|---|
| 1 | 5/95 | 75 | 96 | 94/6 | 69.2 [1.8] |
| 2 | 10/90 | 83 | 97 | 89/11 | 37.8 [1.9] |
| 3 | 15/85 | 80 | 96 | 83/17 | 44.8 [1.6] |
| 4 | 20/80 | 77 | 95 | 82/18 | 46.9 [1.4] |

- The monomer underwent ROP (solvent, melt, organometallic catalyst, tin-based catalyst), reaching $M_n$ > 33,400 g mol$^{-1}$ under industry-relevant conditions, prompting investigation into ROP with L-lactide.




- Reaction conditions were optimised for a range of monomer feeds (Table 1), using $Sn(Oct)_2$ catalyst and 4-MeBnOH initiator.

## 3. Copolymer Microstructure

- Various reaction tracking techniques were used: aliquots analysed by $^1$H NMR spectroscopy, *in situ* $^1$H NMR spectroscopy, and *in situ* FTIR spectroscopy.
- DOSY NMR spectroscopy verified copolymer formation.
- Reactivity ratios were calculated, predicting a **gradient polymeric microstructure**.

| | $r_{LA}$ | $r_{cc}$ |
|---|---|---|
| Aliquots ($^1$H NMR) | 4 | 0.44 |
| *in situ* FTIR | 1.4 | 0.1 |

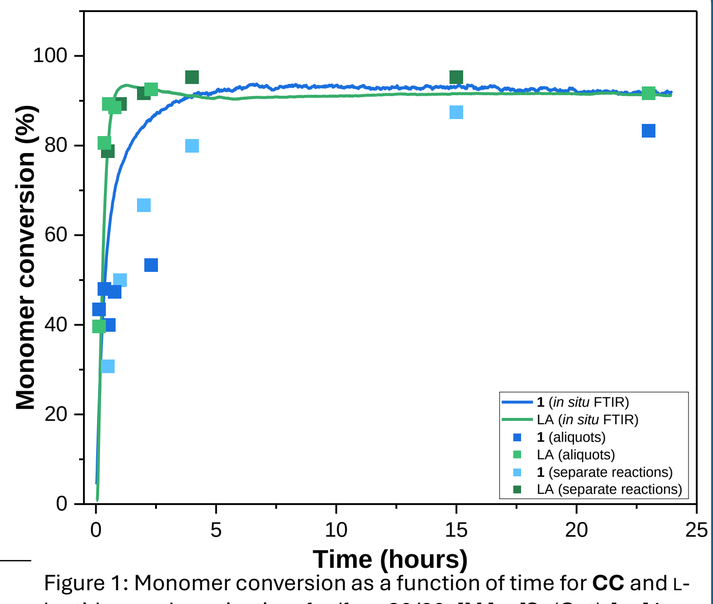



Figure 1: Monomer conversion as a function of time for **CC** and L-lactide copolymerisation: $f_{cc}/f_{LA}$ = 20/80, $[\mathbf{M}_t]_0 : [Sn(Oct)_2]_0 : [4\text{-MeBnOH}]_0$ = 100 : 1 : 2, at 130 °C.




Figure 2: Carbonyl region of $^{13}$C NMR spectrum of poly(LA-*co*-**CC**), showing carbonate (153.8 ppm) and ester (170.0 ppm) linkages.

## 4. Thermal Investigation

- $T_g$ of copolymer increased with increasing carbonate content.

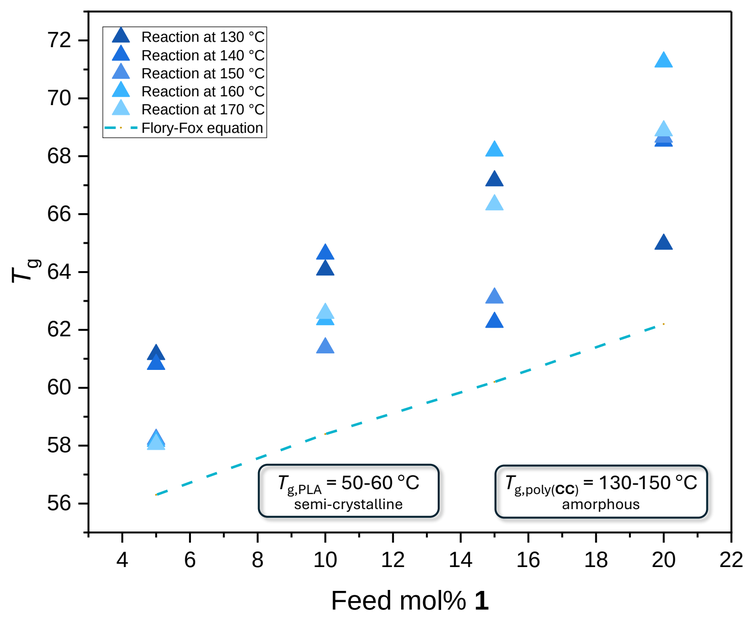



Figure 3: Glass transition temperature ($T_g$) as a function of **CC** content within copolymers formed at various temperatures.

- Films were formed by **thermal pressing** at 150 °C for 5 mins, or **solvent casting** from $CHCl_3$.
- **Crystallinity** was **induced** from amorphous copolymers (higher **CC** content) by thermal processing (Figure 4).

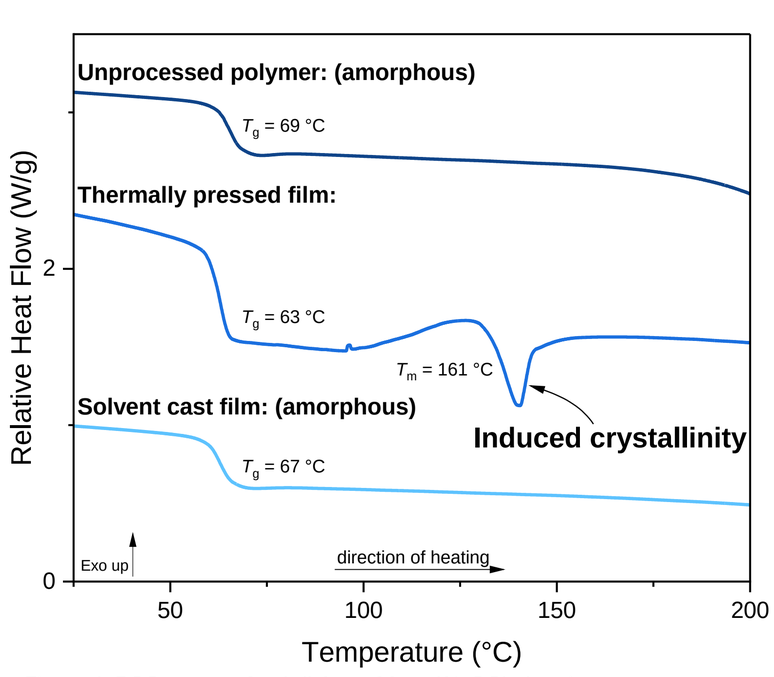



Figure 4: DSC traces of poly(LA-*co*-20 mol%-**CC**) showing heating and cooling from -30 to 230 °C (10 °C min$^{-1}$) of the first heating cycle.

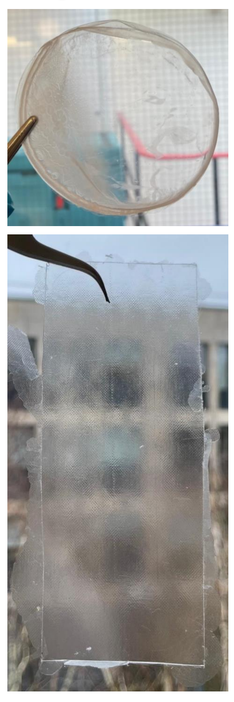
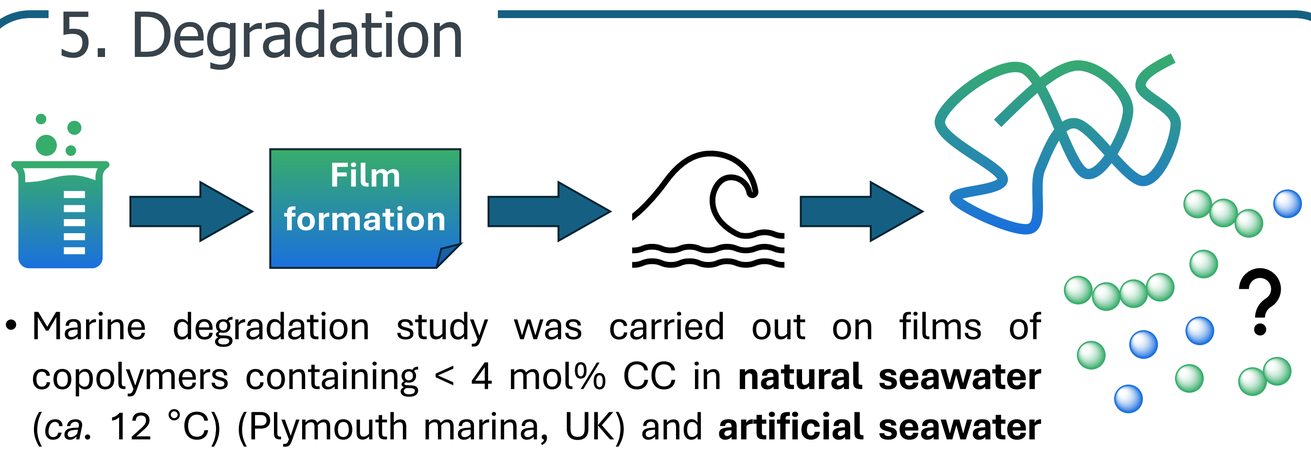


Figure 5: Copolymer films poly(LA-*co*-20 mol%-**CC**): right; solvent cast from $CHCl_3$, far right; thermal press (150 °C, 5 mins).

## 5. Degradation




- Marine degradation study was carried out on films of copolymers containing < 4 mol% CC in **natural seawater** (*ca.* 12 °C) (Plymouth marina, UK) and **artificial seawater** (50 °C).
- **Near total molar mass loss** was seen under accelerated degradation conditions, but not in the natural environment over the course of 9 months.

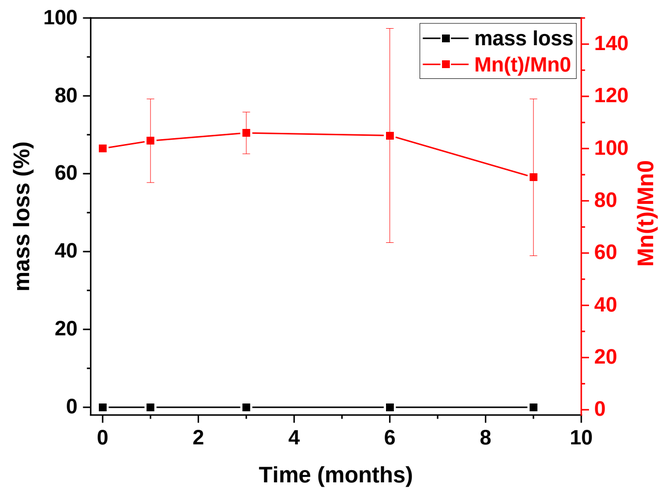



Figure 6: Degradation profile of copolymer in natural seawater (12 °C).

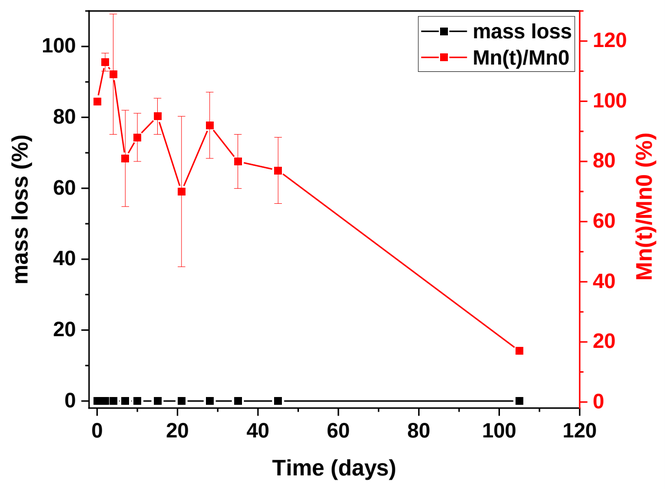



Figure 7: Degradation profile of copolymer in artificial seawater (50 °C).

## 6. Conclusions and Future Work

- Novel, sugar-based cyclic carbonate monomer was investigated in a copolymerisation with L-lactide.
- The resulting copolymers were probed for variations in crystallinity and thermal properties, along with possible changes in degradability.
- Ongoing investigation into the mechanical properties.

- Alternative sugar-based cyclic carbonates are being investigated, to explore introduction of other properties into the copolymer.

## References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