Ring-Opening Polymerisation of Biobased Macrolactones Towards the Circular Economy

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NATURE PROJECT

While **most plastics used for packaging** perform well, they were **not designed with degradability or recyclability** in mind and **account for the largest share of plastic waste** that ends up in landfills and the oceans. **The Nature project aims to develop new grades of polyesters** by taking advantage of their biodegradability and recyclability for use in packaging applications.

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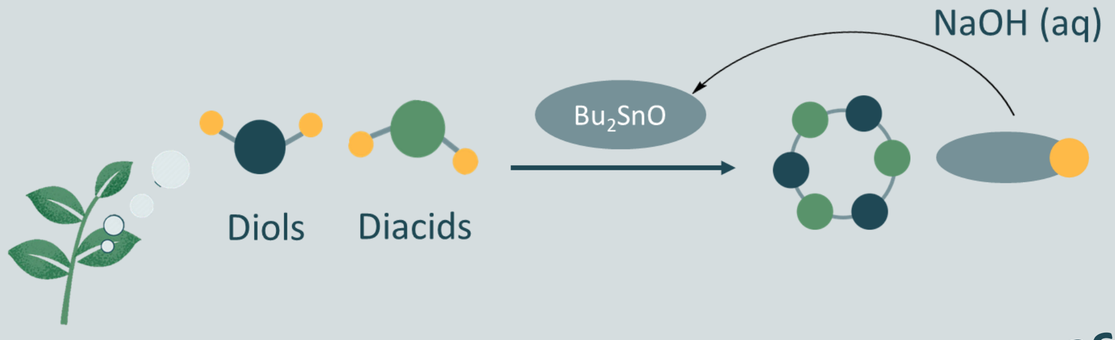
OBJECTIVES

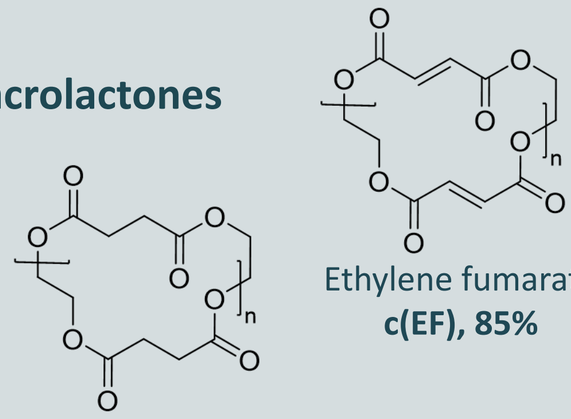
Aliphatic polyesters derived from biomass can be utilized in packaging and biomedical sectors. However, **their production through polycondensation has certain drawbacks.** This study intends to address these issues by exploring **ring-opening polymerization (ROP),** which **can generate high molecular weight polymers under mild reaction conditions without producing any by-products.**

1. Biobased Monomers



- ✓ Diacids and diols used are available from biobased sources.
- ✓ Catalyst can be recovered by hydrolysis.

Macrolactones



2. Polymerisation

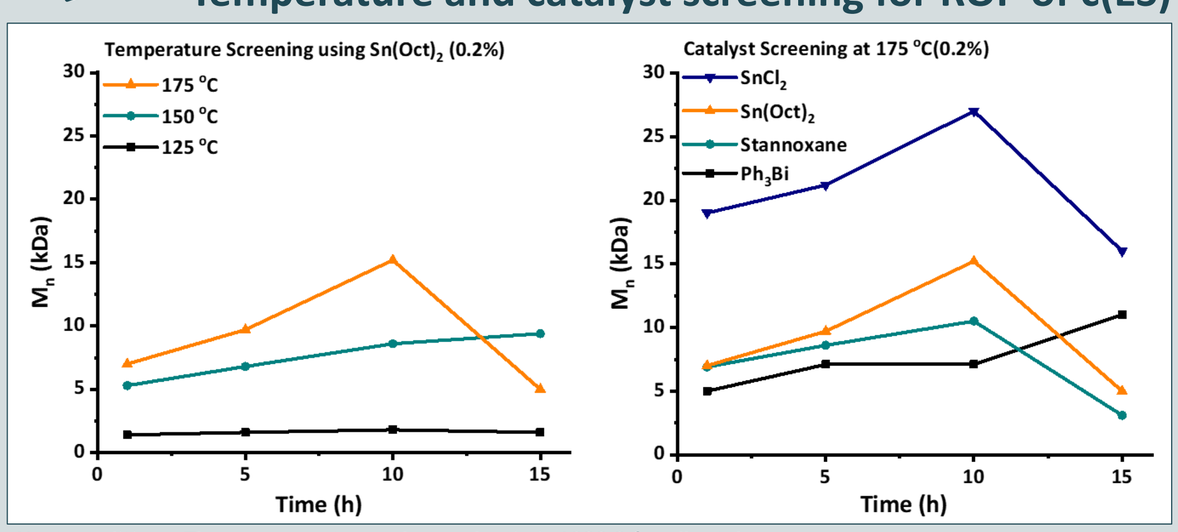
Entropy-driven ROP (ED-ROP)

$\Delta H_p \approx 0$

$\Delta G_p = -T\Delta S_p < 0$

The ROP of strainless macrolactones is entropically driven.

Temperature and catalyst screening for ROP of c(ES)



Neat conditions. The monomer-to-catalyst mol ratio is 1000:2 for all catalysts.
M_n is determined by SEC analysis in $CHCl_3$ (0.5% NEt_3) eluent, calibrated against PS standards.

- ✓ Prolonged reaction time causes a decrease in M_n due to side reactions occurring more prominently.

ROP of c(PS) and c(EF); temperature screening

Monomer	[Cat]:[Init]	$[M]_0$:$[C]_0$:$[I]_0$	Solvent	T (°C)	t (h)	M_n (kDa)[a]	Đ[a]
c(PS)	[TBD]:[BnOH][b]	100:1:1	Toluene	50	48	no conversion	
c(PS)	[TBD]:[BnOH][b]	100:1:1	Toluene	90	25	13.2	1.5
c(EF)[c]	$[Sn(Oct)_2]$	100:0.2	Bulk	150	5	6.3	2
c(EF)[c]	$[Sn(Oct)_2]$	100:0.2	Bulk	175		crosslinked	

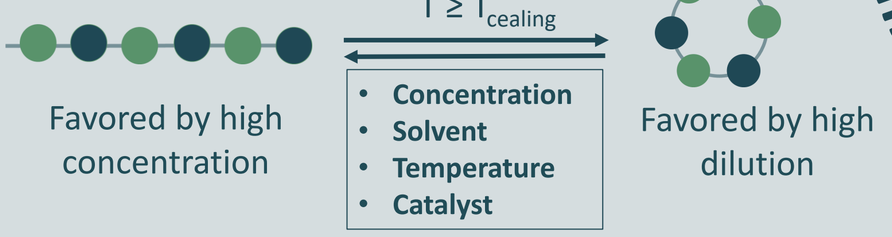
[a] M_n and Đ are determined by SEC analysis in $CHCl_3$ (0.5% NEt_3) eluent, calibrated against PS standards.
[b] Triazabicyclodecene (TBD) is used as the catalyst, and benzyl alcohol (BnOH) is used as an initiator.
[c] 3 wt% 4-methoxy phenol is used as a radical scavenger in the polymerisation of c(EF).

- ✓ Unlike the other macrolactones, c(PS) can polymerise using an organo-catalyst at 90 °C, possibly due to the contribution of side groups to ring strain.

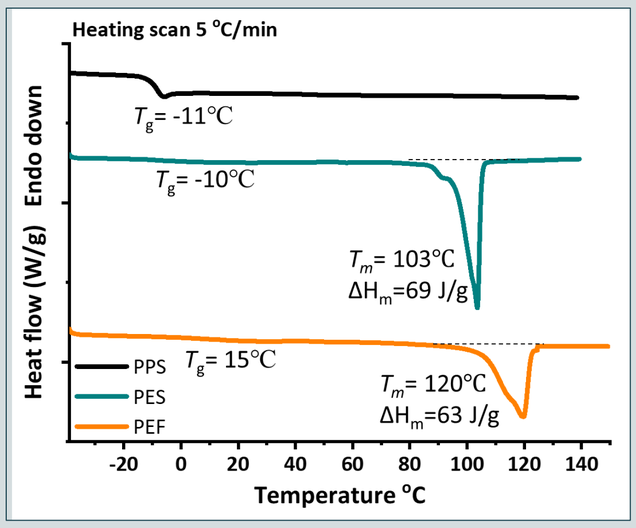
3. Chemical Recycling

FUTURE WORK

Ring-Chain Equilibria



In solutions, polyesters exist in an equilibrium between cyclic and linear forms. **Controlling the reaction conditions makes it possible to shift the equilibrium to cyclic compounds**, which will enable a closed-loop process.

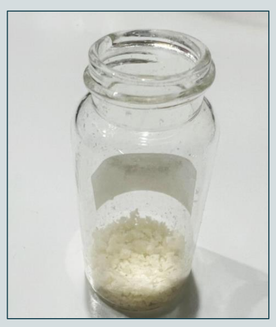


Properties of polymers

- ✓ PPS is amorphous due to irregular pendant groups along the backbone.
- ✓ PEF exhibits the highest T_g and T_m due to its rigidity.

Following polymerisation optimisation, further studies will examine their barrier properties.

Poly (propylene succinate)
PPS



Poly (ethylene succinate)
PES

Poly (ethylene fumarate)
PEF

CONCLUSION

- ✓ Neat conditions, higher temperatures and metal-based catalysts are necessary to achieve higher M_n for ED-ROP of c(ES), while c(PS) can polymerise at lower temperatures.
- ✓ ROP of c(EF) must be studied further as long reaction time and high temperature cause cross-linking. It has a more rigid structure than others.

TAKE HOME

- ✓ PES can be produced through ROP, similar to its commercial grades.
- ✓ PEF is a novel polyester; the double bonds in its backbone offer various possibilities for post-functionalisation to confer specific properties upon the polyester or directly cross-linked.

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