

# Polymers from cellulosic waste:

Direct polymerisation of levoglucosenone using DBU as a catalyst

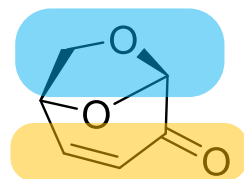


**Mr. Brett Pollard**, Dr. Michael G. Gardiner, Prof. Dr. Martin G. Banwell, Prof. Dr. Luke A. Connal

*ChemSusChem* 2023

*38APS Auckland, New Zealand*

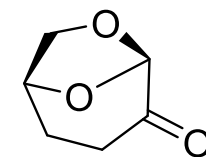
# Levoglucosenone: A Platform for Chemistry



Levoglucosenone

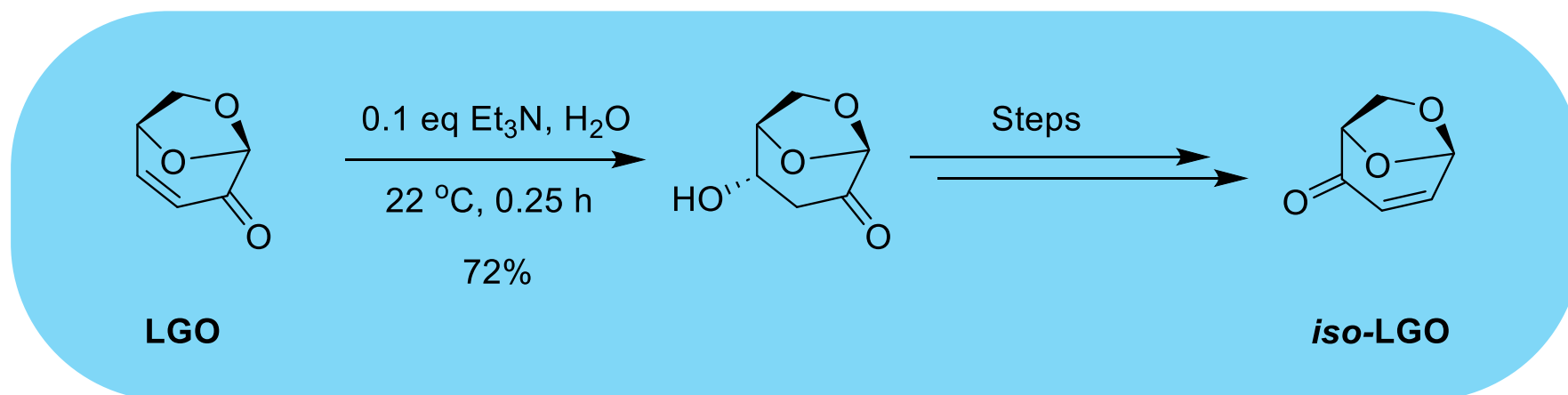
Defined stereochemistry

Reactive Michael acceptor

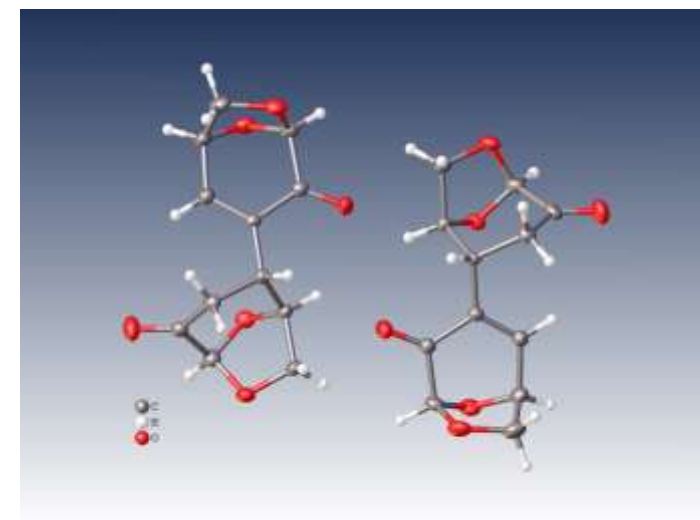
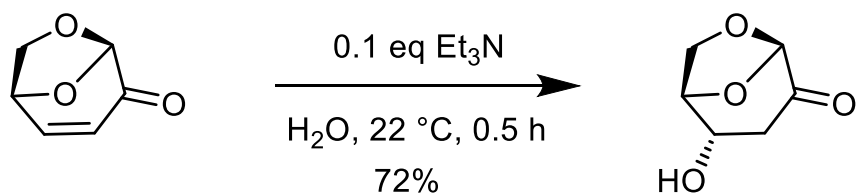


Kiloton scale

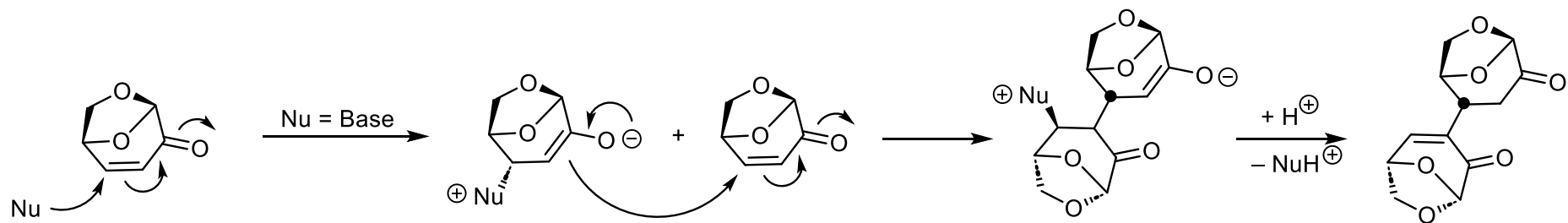
# Making *iso*-LGO – Hydration Reaction



# An Interesting Side Reaction: Dimerisation

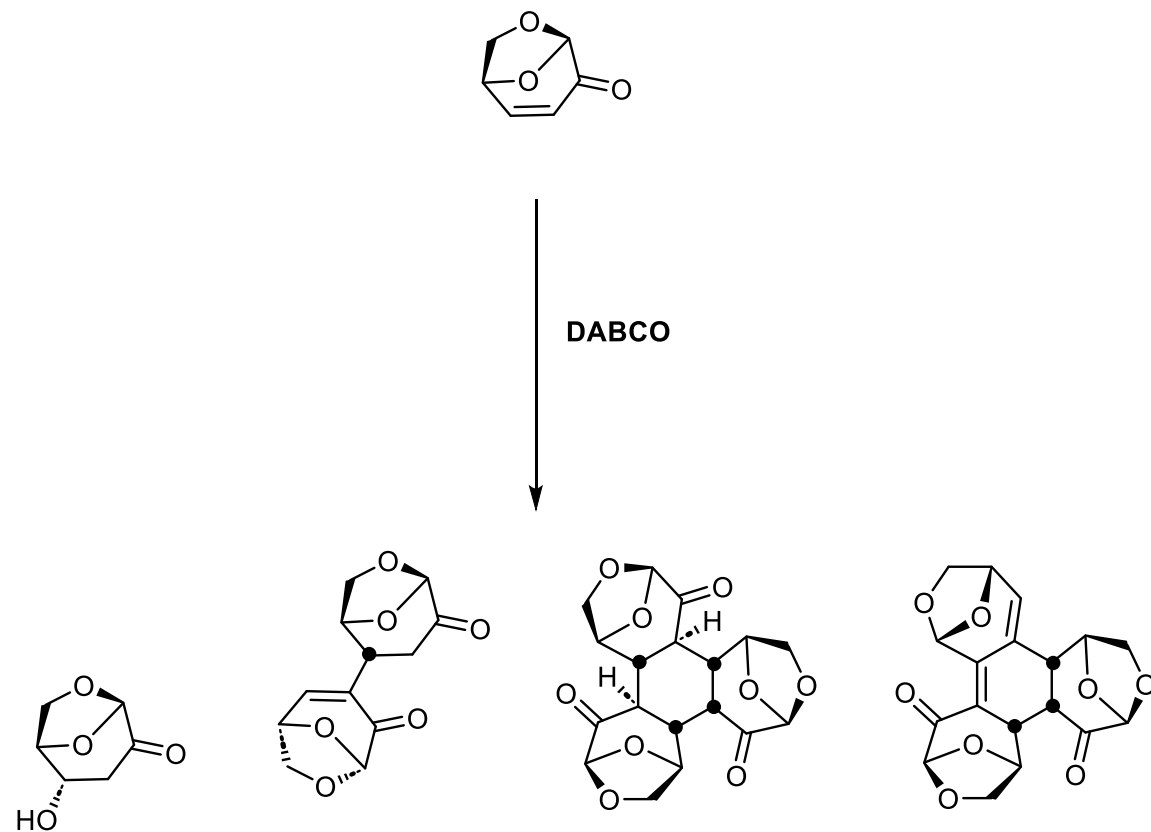
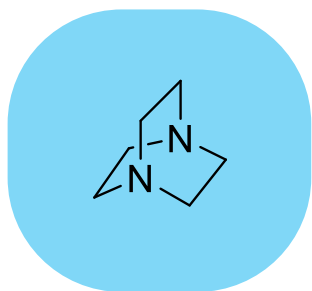
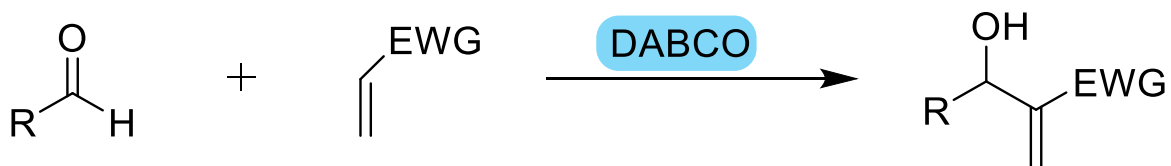


# Considering the Addition Mechanism



# Finding a Suitable Nucleophile: **DABCO**

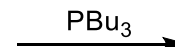
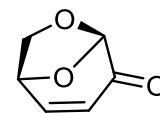
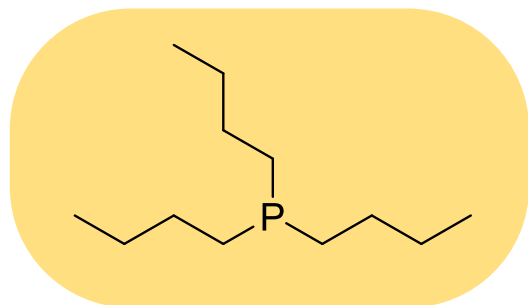
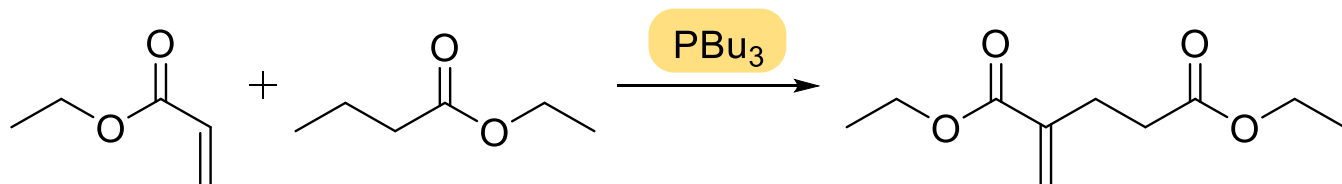
## Morita-Baylis-Hillman



No Polymer Formed – Just the Usual Suspects

# Identifying a Suitable Nucleophile: **PBu<sub>3</sub>**

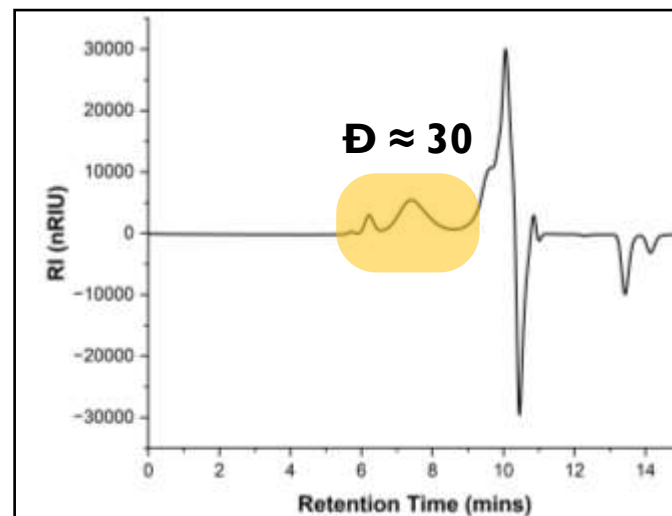
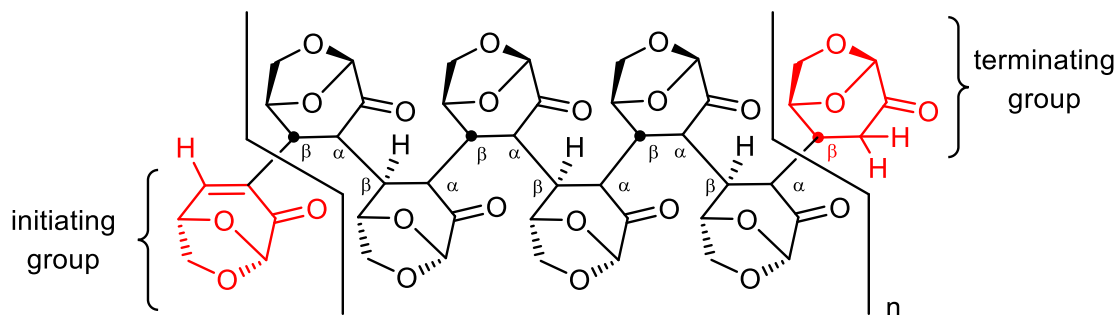
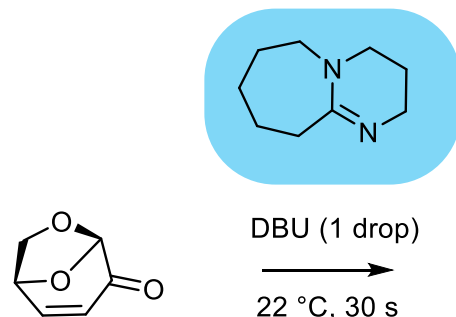
## Rauhut-Currier



Some Polymer Formation (<5%)  
+ The Usual Suspects



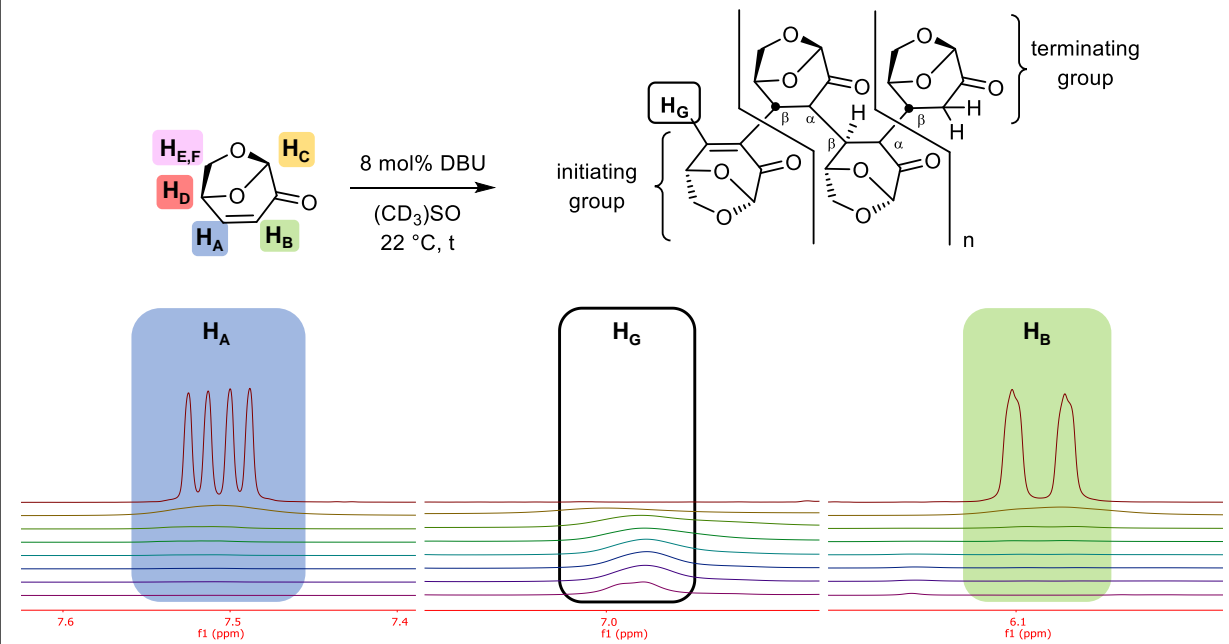
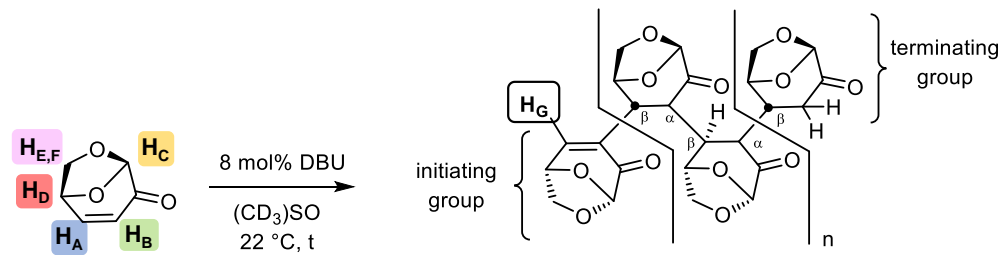
# Identifying a Suitable Nucleophile: **DBU**



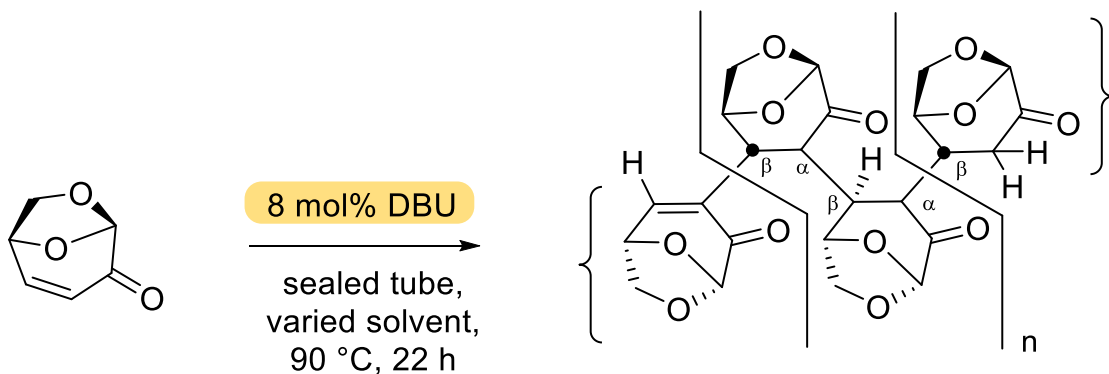
**Polymer!**



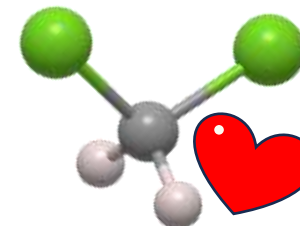
# Probing the Mechanism



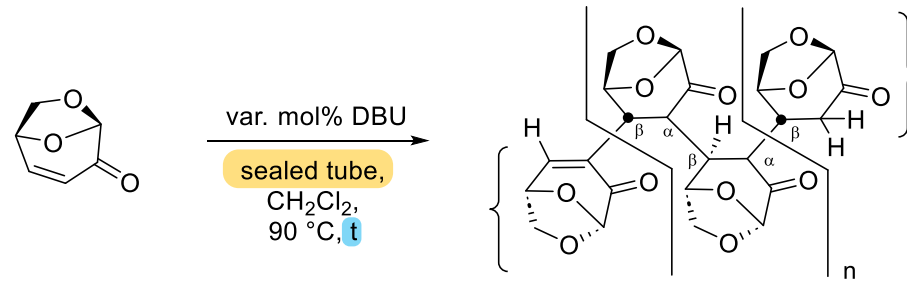
# Improving Dispersity: Solvent Choice



Solvent	Result
Solvent free	Rapid, poor conversion & control
Cyrene <sup>®</sup>	Aldol problems
Water	Solidification – rapid side product formation
Acetone	Generates polymer, poor dispersity
Dichloromethane	Best conversion, best dispersity



# Optimising Reaction Time & Catalyst Loading



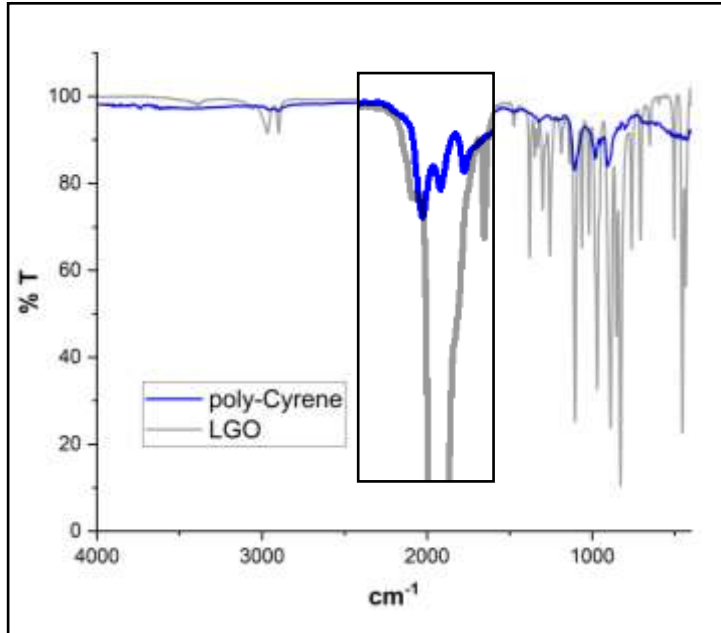
**Time**

Entry	Reaction Time (h)	Catalyst Loading (mol%)	Recovery/Conversion (%)	M <sub>n</sub> (kDa)	Dispersity (Đ)
a	4	8	85	62	9.9
b	21	8	100	278	3.9
c	30	8	84	246	4.2
d	69	8	73	83	8.4

**Cat. Loading**

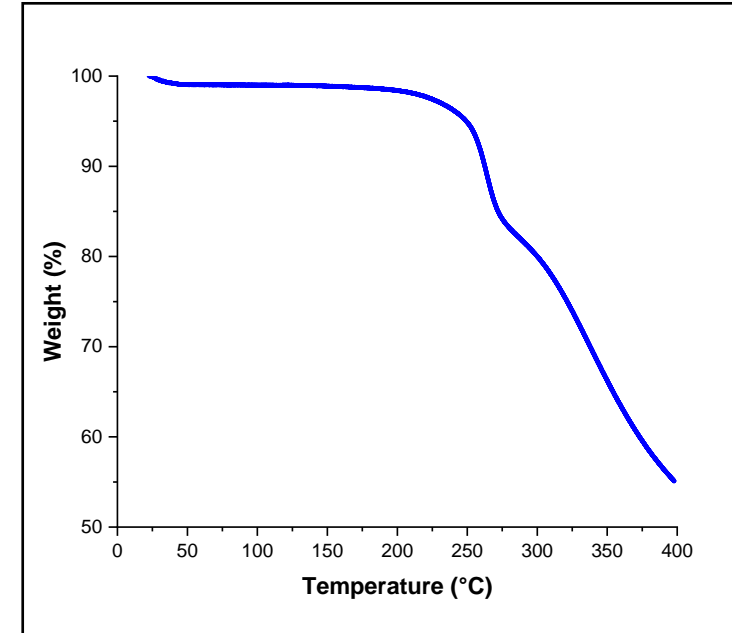
Entry	Reaction Time (h)	Catalyst Loading (mol%)	Recovery/Conversion (%)	M <sub>n</sub> (Da)	Dispersity (Đ)
e	21	8	100	278	3.9
f	21	4	100	140	3.3
g	21	2	83	236	2.4
h	21	1	81	167	3.0

# Characterising poly-Cyrene: A Challenge



## FT-IR

**C=O increase in wavenumber  
consistent with loss of  $\alpha,\beta$ -alkene**



## TGA

**$T_{D5\%}$  at 249  $^{\circ}\text{C}$   
 $T_{D50\%}$  >400  $^{\circ}\text{C}$**

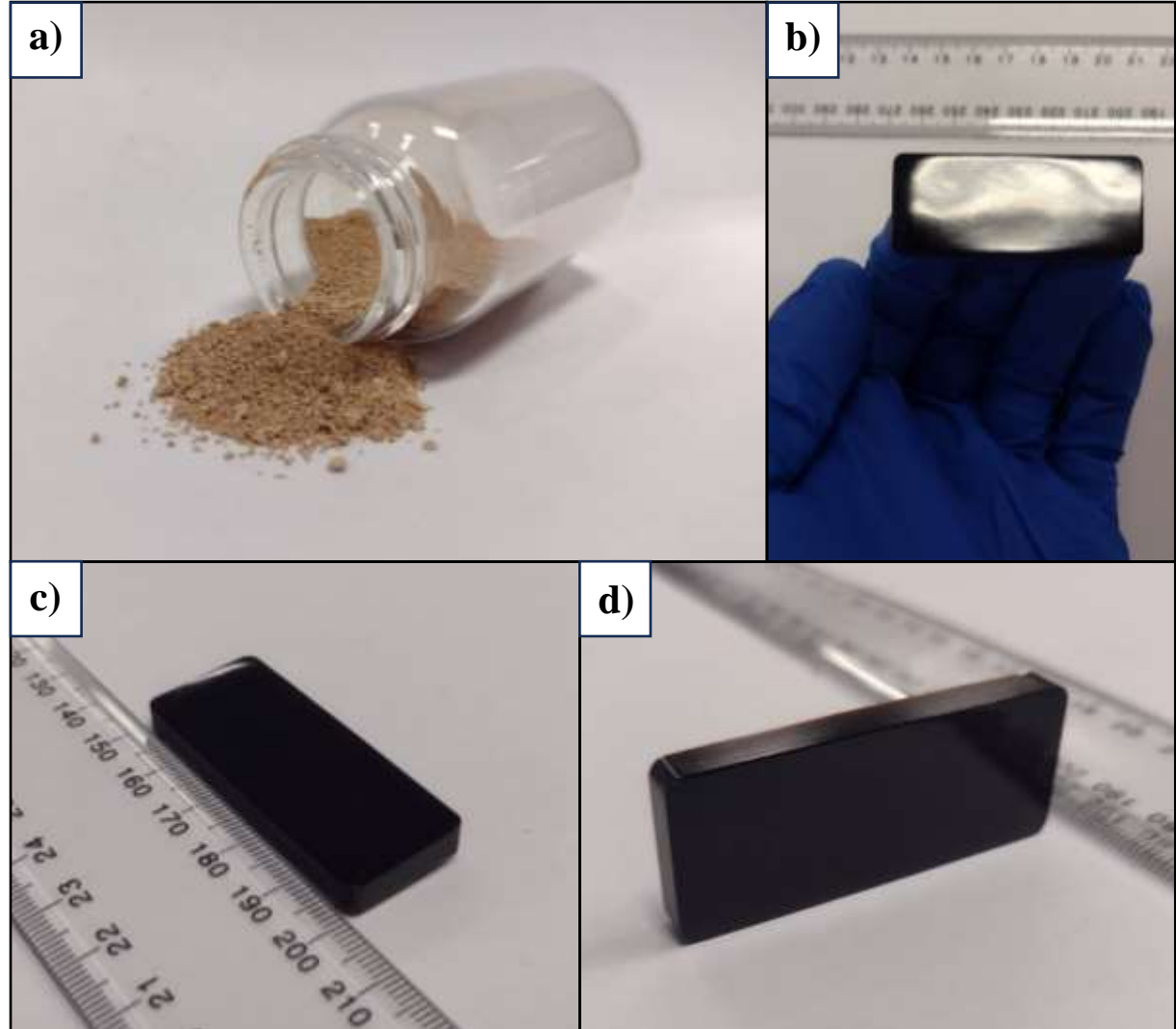
# Precipitation & Casting from DMSO



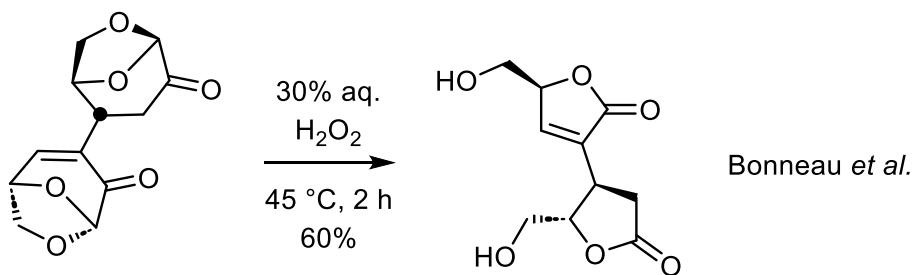
**Precipitate into  
Chilled, Poor Solvent**



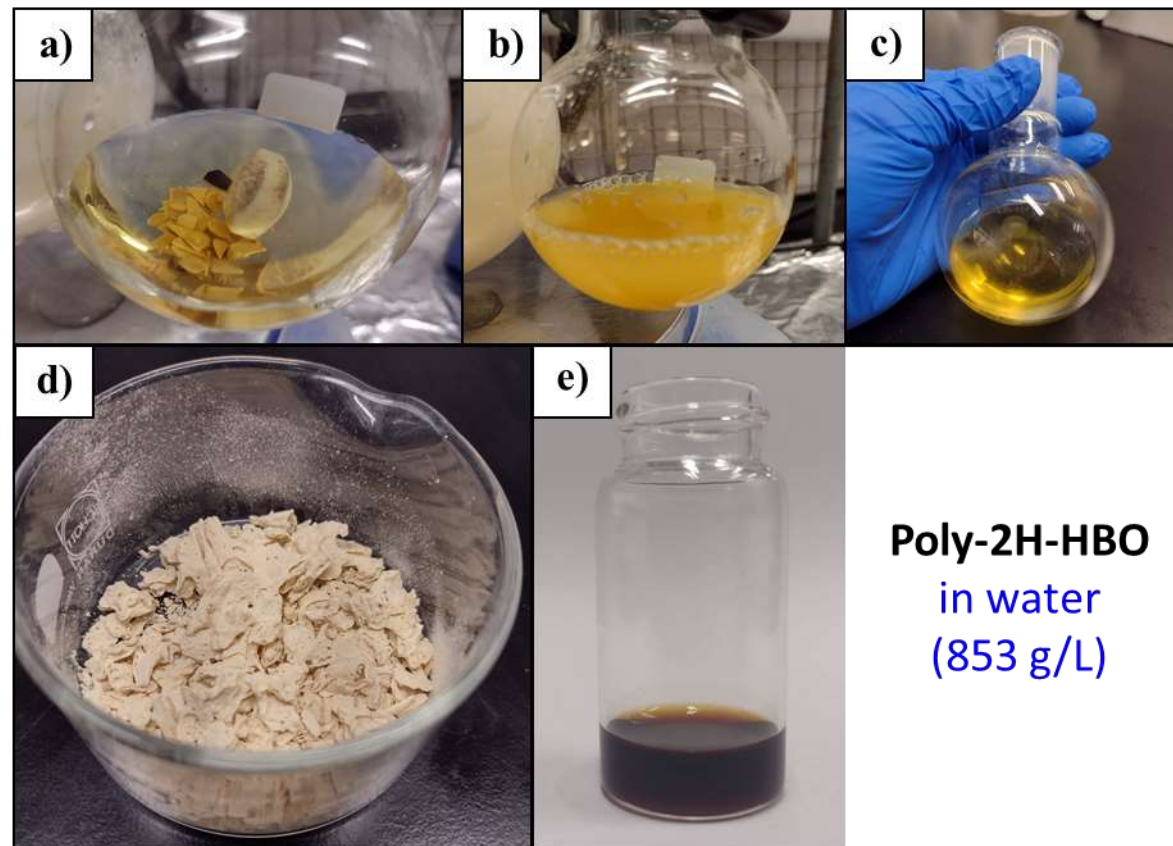
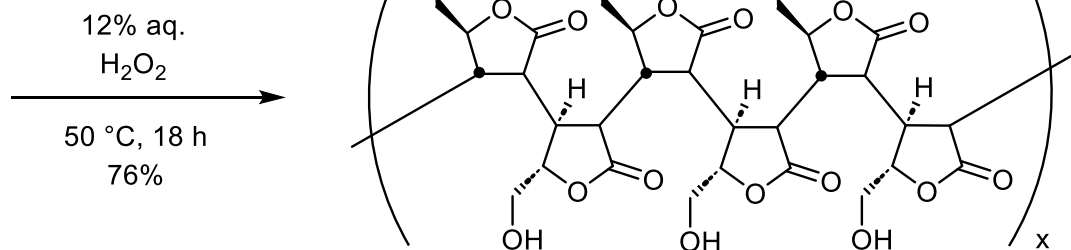
**Collect by Filtration,  
Wash**



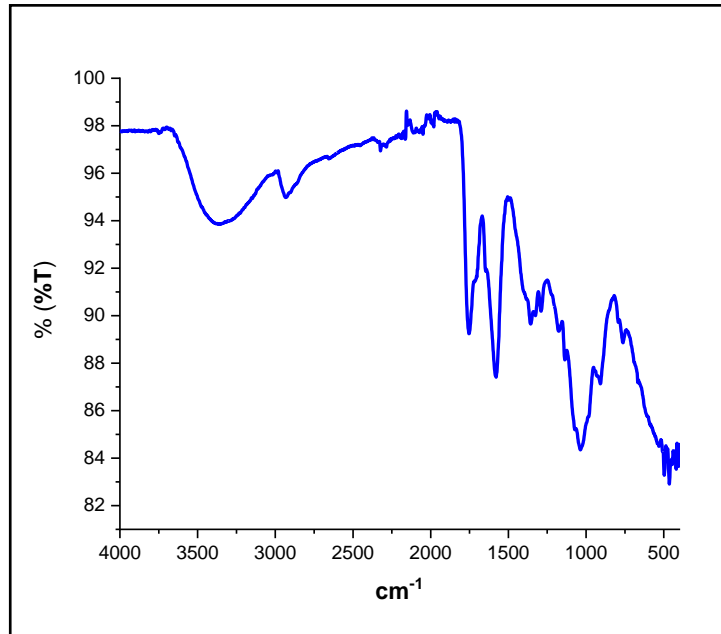
# Functionalisation: Baeyer-Villiger Oxidation



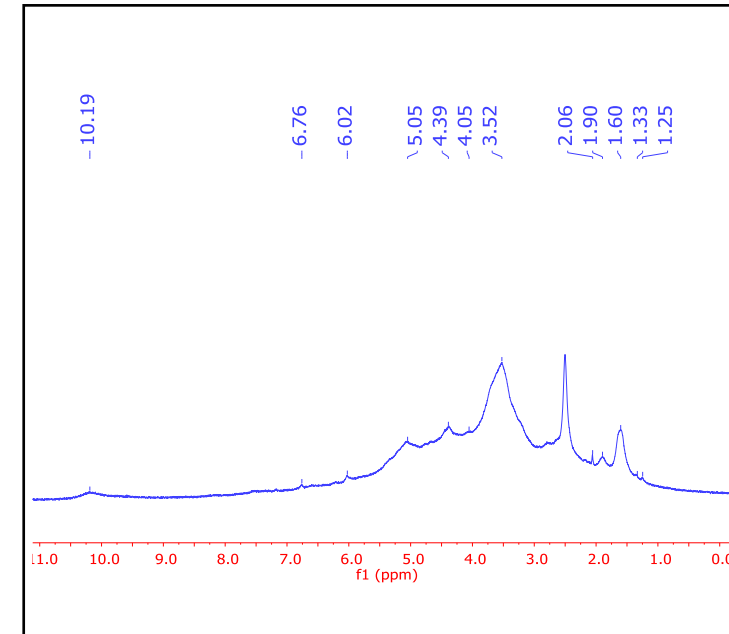
"poly-Cyrene"



# Poly-2*H*-HBO: Analysis Shows Transformation

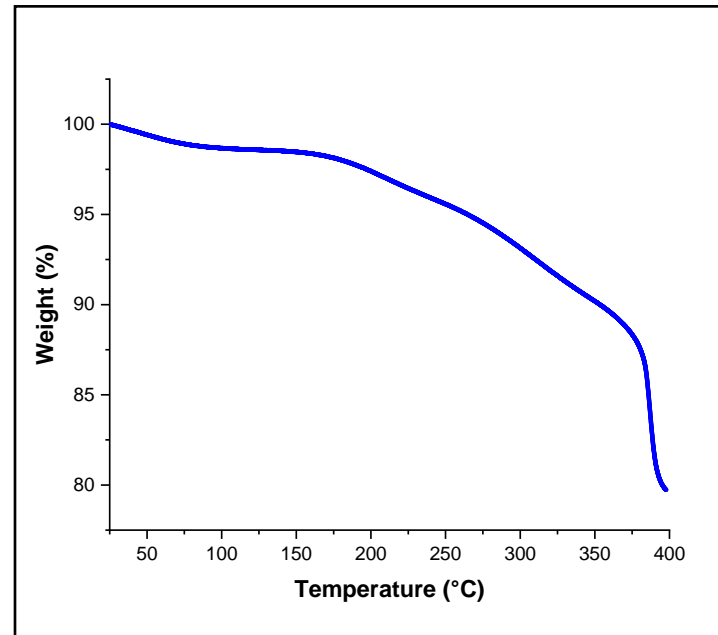


**FT-IR**  
Strong -OH stretching band  
C=O indicative of  $\gamma$ -lactone



**<sup>1</sup>H NMR**  
Intense signal  $\delta$  3.52 repeat unit

# Poly-2*H*-HBO: A Thermally Stable Product



**TGA**  
**T<sub>D5%</sub> at 265 °C**  
**T<sub>D50%</sub> >400 °C**



# Assessing Polymer Morphology

**Amorphous**



*Morphology*



*Expected PXRD Trace*

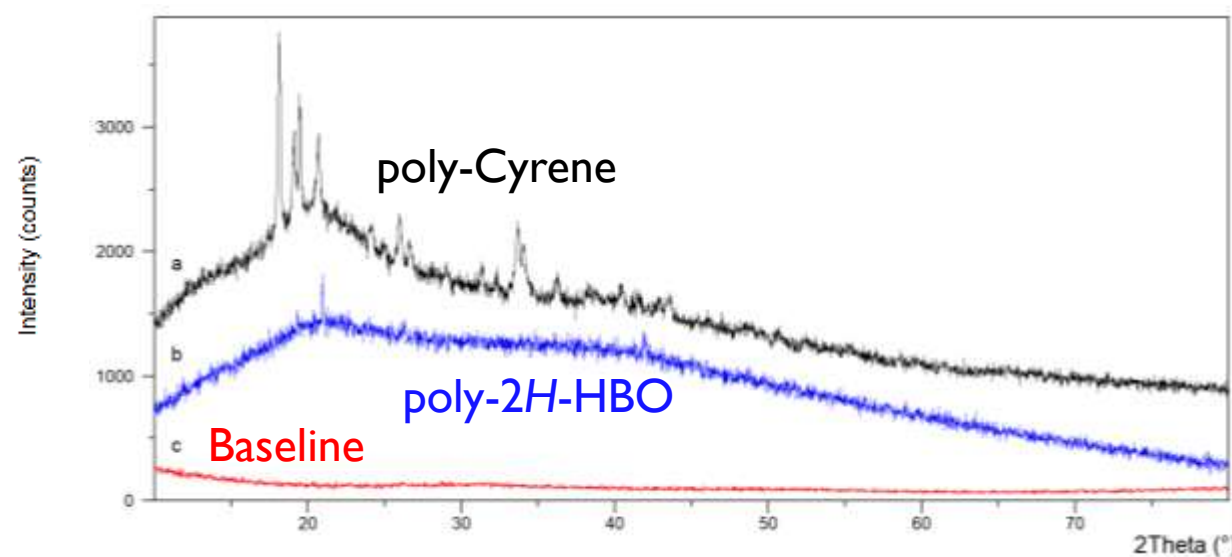
**Crystalline or Semi-Crystalline**



*Morphology*



*Expected PXRD Trace*



# Conclusions

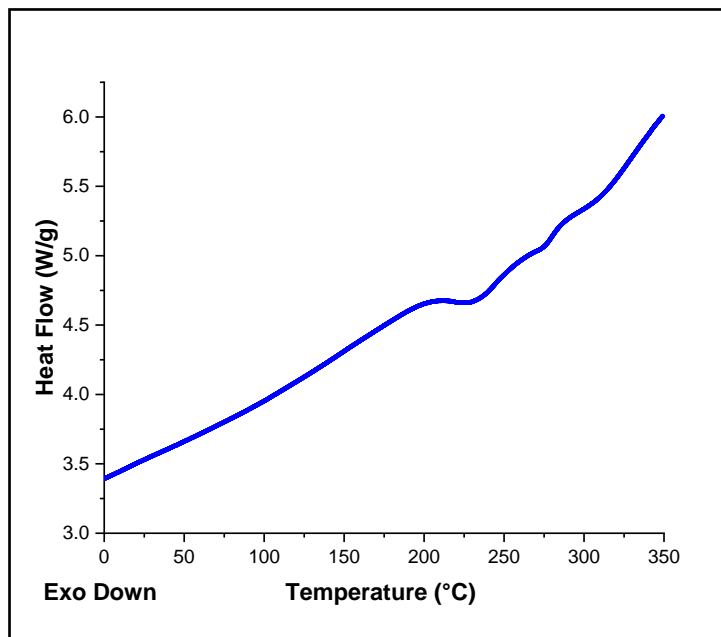
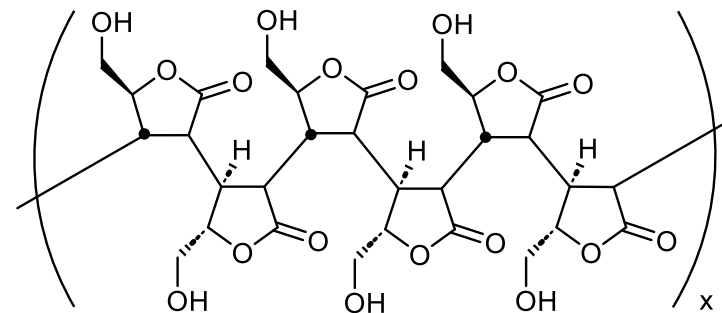
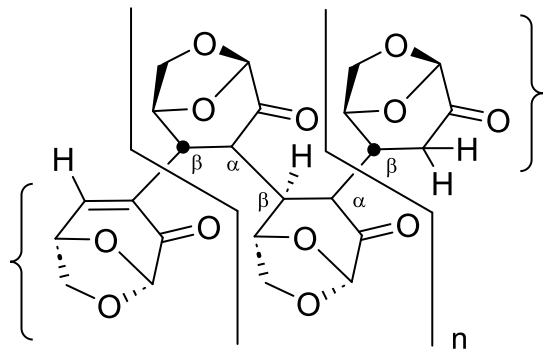
- Atom economic, one-step and high yield polymerisation of LGO
- High molecular weight product with good thermal stability
- Easily scalable
- Scope for functionalisation

Have a chat or contact me at:

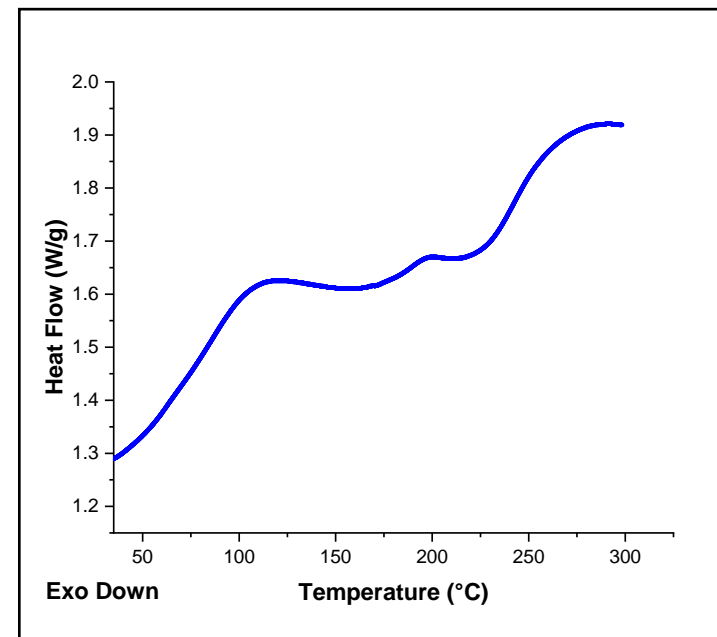
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Australian  
National  
University



**DSC**  
**Exotherm at 235 °C**  
**Consistent with  $T_D$**



**DSC**  
**Exotherms at 114 °C, 200 °C**  
**No clear  $T_g$  below decomposition**