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NATURE

Nature-like circularly recyclable polyhydroxyalkanoates with improved physical properties

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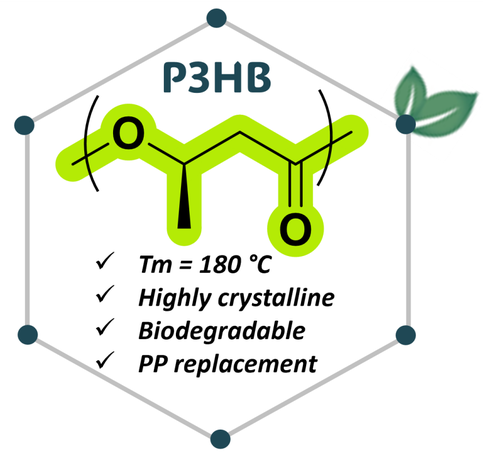
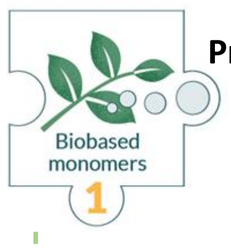
Overview and concept

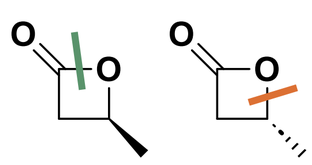
Poly(3-hydroxybutyrate) **(P3HB)** is a naturally produced biocompatible polyester that has gained attention as a biodegradable alternative to isotactic-polypropylene (*i*PP), especially for **better end-of-life food packaging applications.**[1] These polymers can be synthesised from the ring-opening polymerisation (ROP) of cyclic 8-membered diolide monomer (8DL^{Me}) using metal-based catalysts, however, **simple organic catalysts** are greener alternatives to those currently used.[2,3] They are also less toxic, have greater stability in ambient environments, are readily available and cheap.[4] Here, the improved synthesis of 8DL^{Me} using microwave reactor and subsequent screening of organocatalysts for the ROP of 8DL^{Me} is shown.



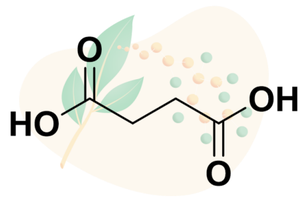
8DL^{R} Monomer synthesis



Previously: *β*-butyrolactone *for P3HB*



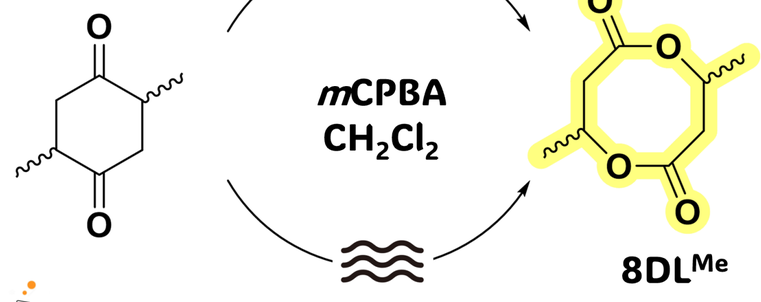
Problematic during ROP due to competing ***O*-acyl** and ***O*-alkyl** cleavage. Results in dead chain ends and poor polymer mechanical properties.



Succinic acid

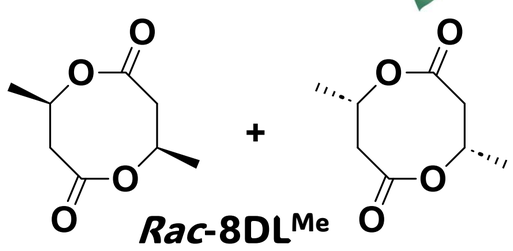
1,2,3

1. *NaOMe, MeOH, Reflux*
2. *K_2CO_3, MeI, Acetone, RT*
3. *aq H_2SO_4, Reflux*



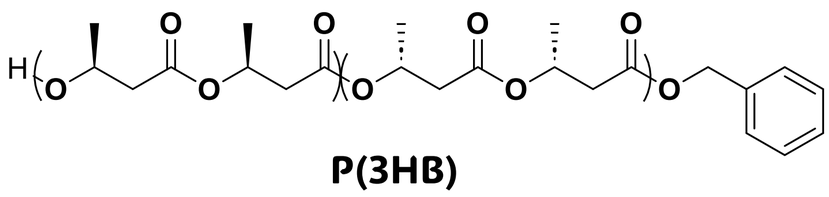
Conventional: **48 h, RT** Microwave: **3 min, 80 °C**

Organocatalyst Screening



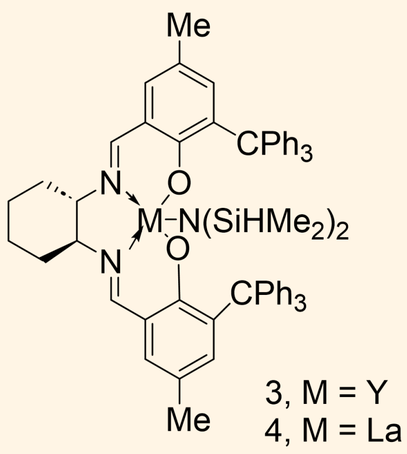
Catalyst

BnOH



P(3HB)

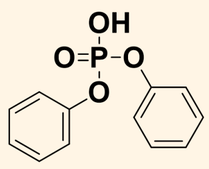
M **Metal-catalyst**



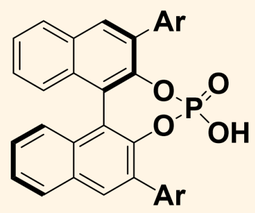
3, M = Y
4, M = La

- ✓ *High activity*
- ✓ *stereoselectivity*
- × *Lengthy synthesis*
- × *Toxic, unstable*
- × *Expensive*

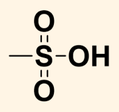
AH **Organic acid**



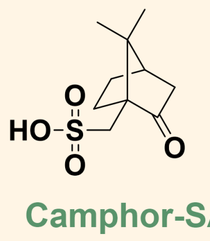
DPP



Trip-BINOL



MSA



Camphor-SA

- ✓ *Readily available*
- ✓ *cheap and stable*
- ✓ *Less toxic*
- ≈ *Comparable activity*
- ≈ *Stereoselectivity*

	Catalyst	[M]:[Cat]:[I][a]	Solvent	Temp (°C)	Time[b] (days)	$M_{n,NMR}$ [c] (g.mol^{-1})	Conv[d] (%)
1	DPP	50:5:1	$CHCl_3$	40	7	4700	55
2	Trip-Binol	60:1:1	$CHCl_3$	40	11	7220	70
3	Trip-Binol	60:1:1	Toluene	60	4	8900	80
4	MSA	50:5:1	$CHCl_3$	RT	2 h	7000	80
5	MSA	50:5:1	$CHCl_3$	RT	24 h	7900	92
6	MSA	50:1:1	$CHCl_3$	RT	48 h	7500	88

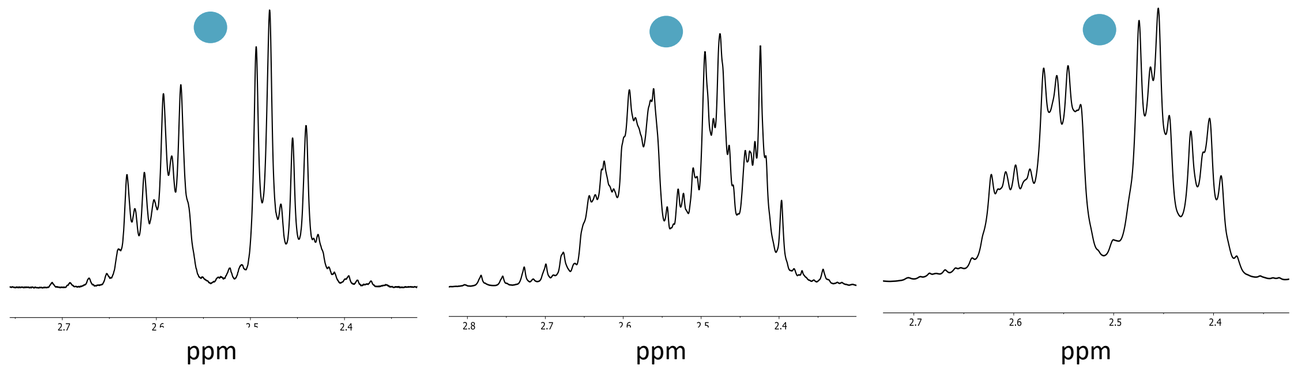
[a]All polymerisations were conducted with a target DP of 50 and target molecular weight of 8600 g mol^{-1}. [b]The polymerisations were run for days (d) or hours (h). [c]$M_{n,NMR}$ and conversion were tracked with ^{1}H NMR using the methyl signal of the monomer and polymer at 1.5 and 1.2 ppm respectively. [d]Conversion is determined as the percentage of monomer that has ring opened both with polymerisation and other side reactions.

Catalyst choice affects the polymer **tacticity**, which impacts the final **physical properties** and **potential applications**

Run 3
Improved selectivity
Poor rate (4 days)

Run 5
Poor selectivity
Improved rate (2h)

Run 6
Better selectivity
Reduced rate (48 h)



^{1}H NMR Spectrum (300 MHz, $CDCl_3$) of P3HB in the methylene region

Conclusions & Future work

- 8DL^{Me} synthesis using microwave reactor reduced reaction time from **48 h to 3 min**.
- Organic acids catalysed ROP of 8DL^{Me} with different rates and selectivity. MSA exhibited highest rate while trip-binol showed the best stereoselectivity.
- **Future:** Chiral sulfonic acid catalysts (Camphor-SA) for ROP

References

1. A. H. Westlie, E. C. Quinn, C. R. Parker and E. Y. X. Chen, *Prog. Polym. Sci.*, 2022, **134**.
2. X. Tang, A. H. Westlie, E. M. Watson and E. Y. Chen, *Science*, 2019, **366**, 754-758.
3. X. Tang and E. Y. Chen, *Nat Commun*, 2018, **9**, 2345.
4. B. Koca, D. Akgul and V. Aviyente, *Eur. Polym. J.*, 2019, **121**, 109291.

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