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Biobased & Biocatalysed Covalent Adaptable Networks

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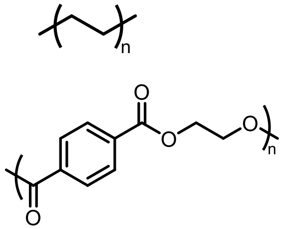
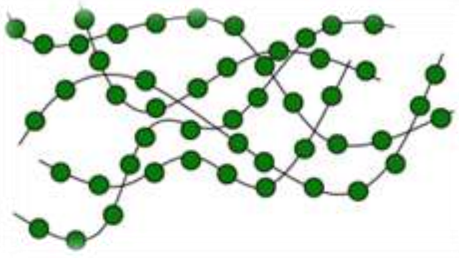
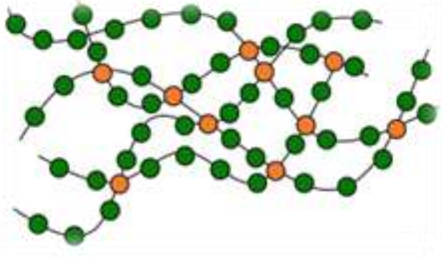
Covalent Adaptable Networks: A Third Family of Polymer

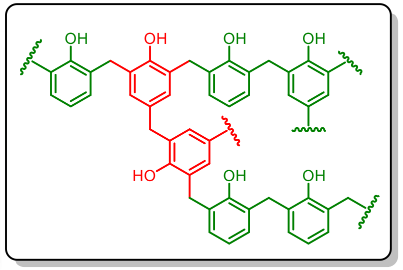
Thermoplastics

Thermosets







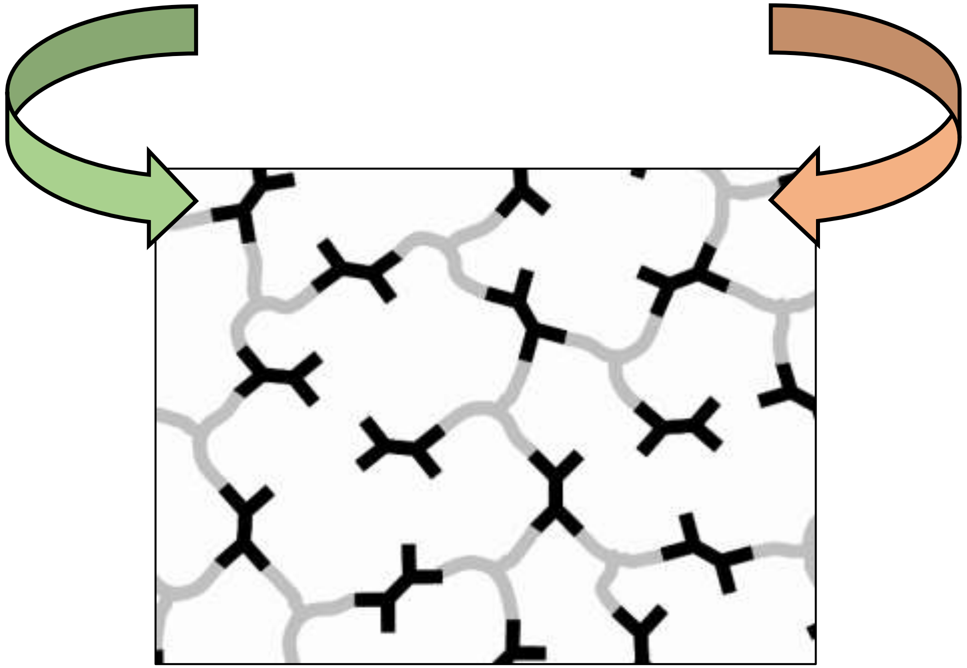


Linear polymer chains
Flow upon heating (T > T_g or T_m)
Dissolve in good solvent

Crosslinked networks
Do not flow nor dissolve
(swell in good solvent)

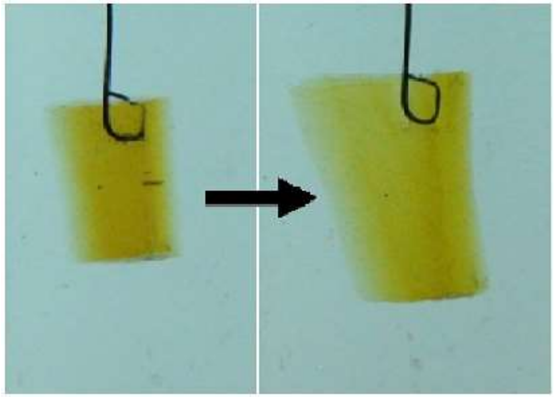
Recycling & Reshapable

Recyclable & Reshapable
Poor chemical resistance
& mechanical properties



Covalent Adaptable Networks (CANs)

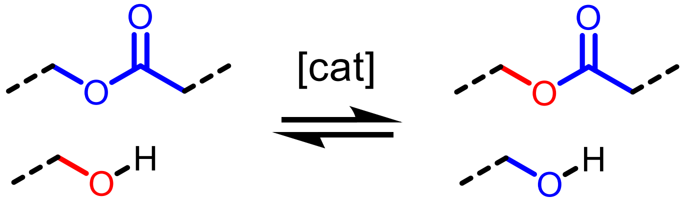
Not Recyclable & Reshapable
Excellent chemical resistance
& mechanical properties

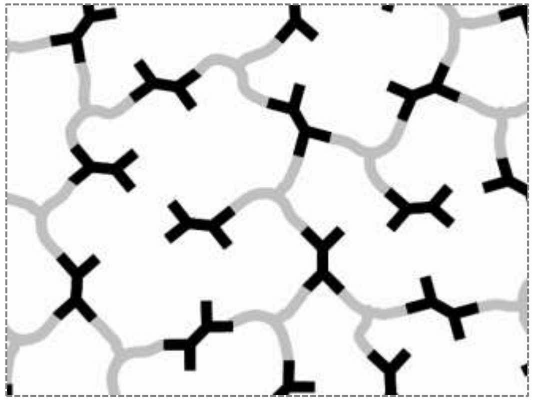


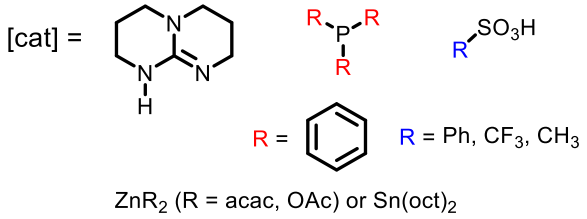
Science **2011**, 334, 965–968.
Science **2002**, *295*, 1698–1702.

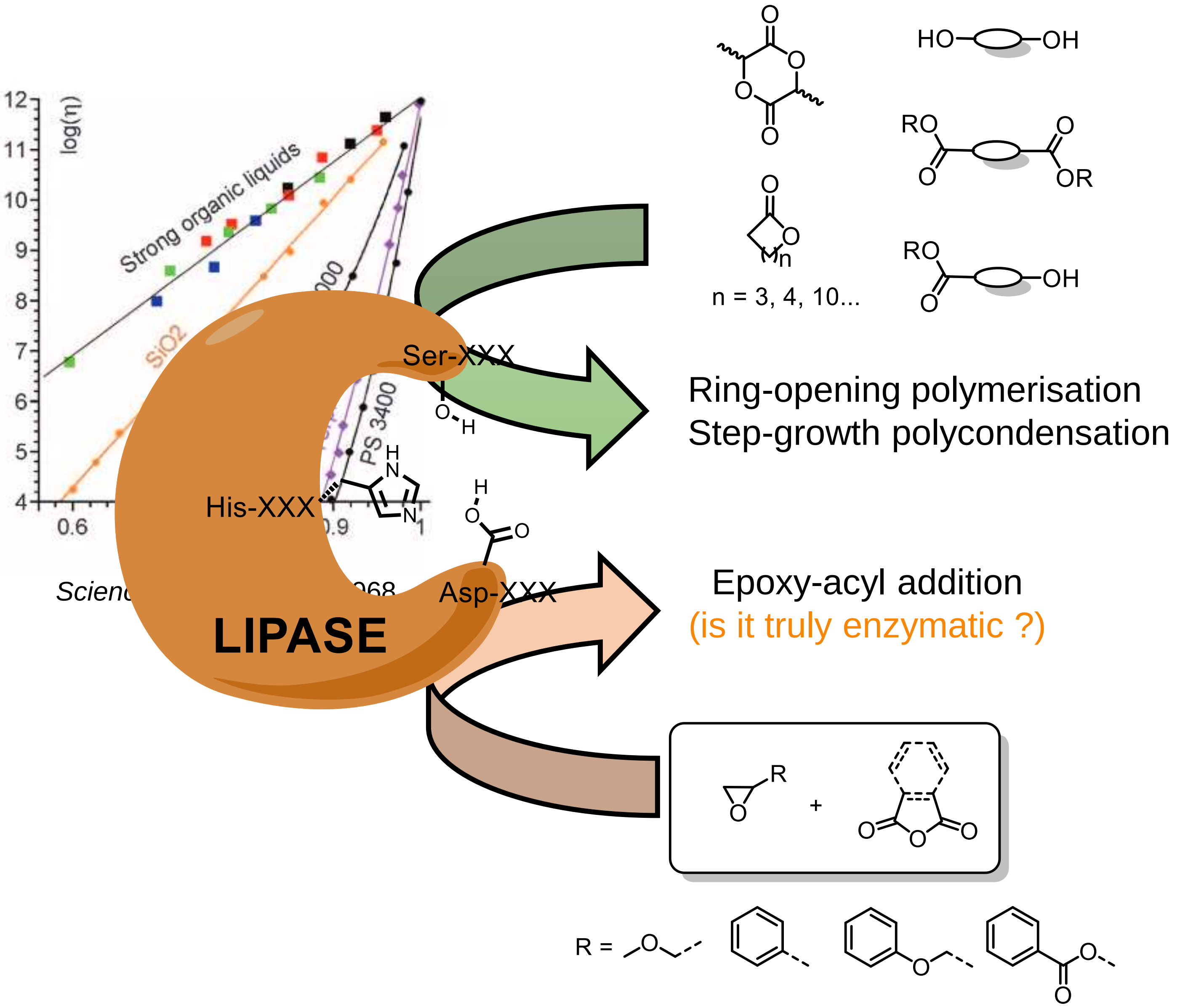
Transesterification-based vitrimers

Transesterification





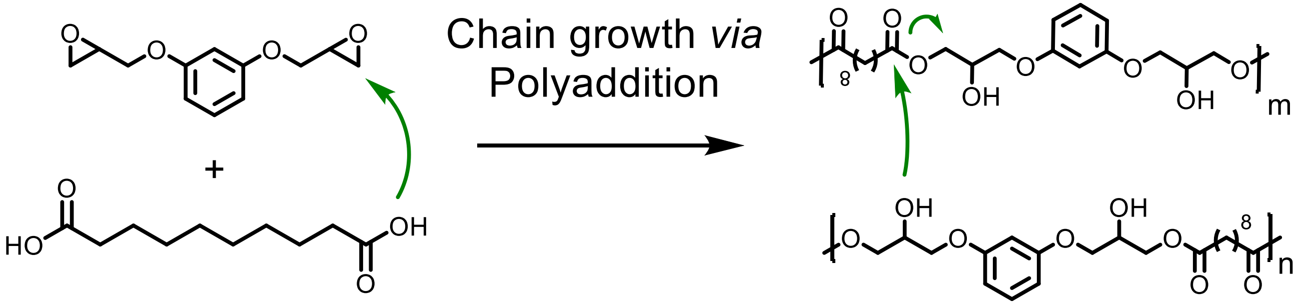


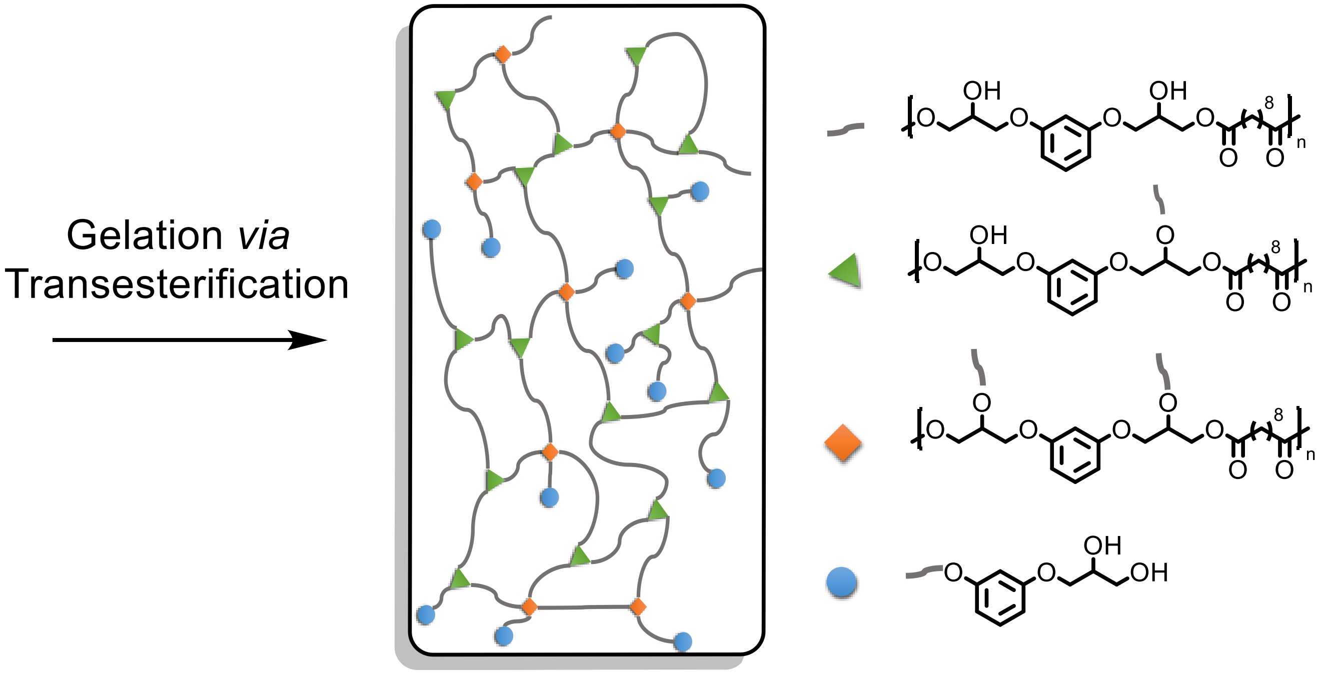


ACS Macro Lett. **2012**, 1, 789−792
ACS Macro Lett. **2018**, 7, 817−821

Macromol. Rapid Commun. **2016**, *37*, 1996−2004
Macromol. Biosci. **2002**, *2*, 429 – 436

Epoxy-Acid networks: polymerisation/crosslinking mechanism and features





Gelation

$$\overline{f_B} = \frac{\sum_{i=0}^{4} n_i \cdot i^2}{\sum_{i=0}^{4} n_i \cdot i} = 2.5$$

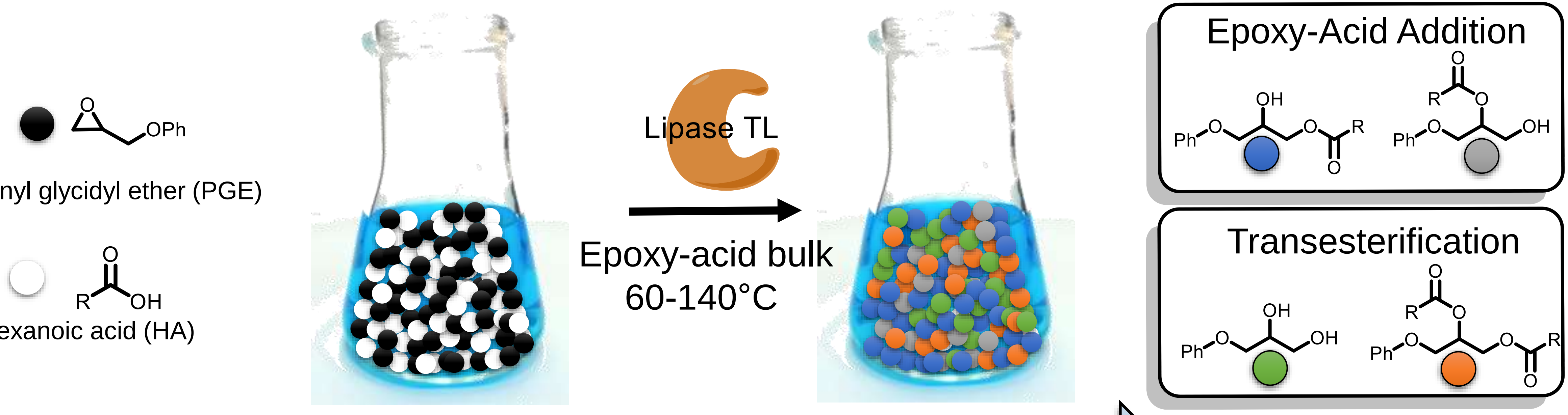
$\overline{f_B}$: average functionality
n_i : isomer probability
i : isomer functionality

Classical catalyst
organic (imidazole-based, TBD, phosphines)
organometallic (Sn-based, Zn-based etc.)

Conditions
bulk (mixture of acid and epoxide)
high temperature (130°C-180°C)

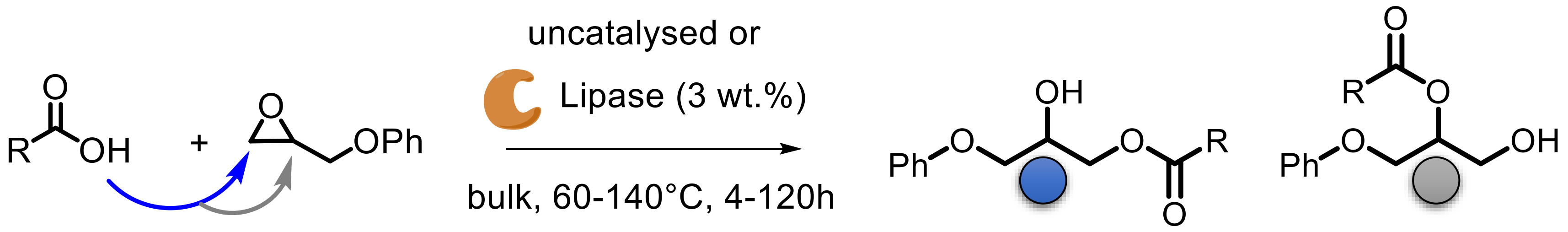
Science **2011**, 334, 965–968.
ACS Macro Lett. **2012**, 1, 789−792

From model molecule studies to network build-up



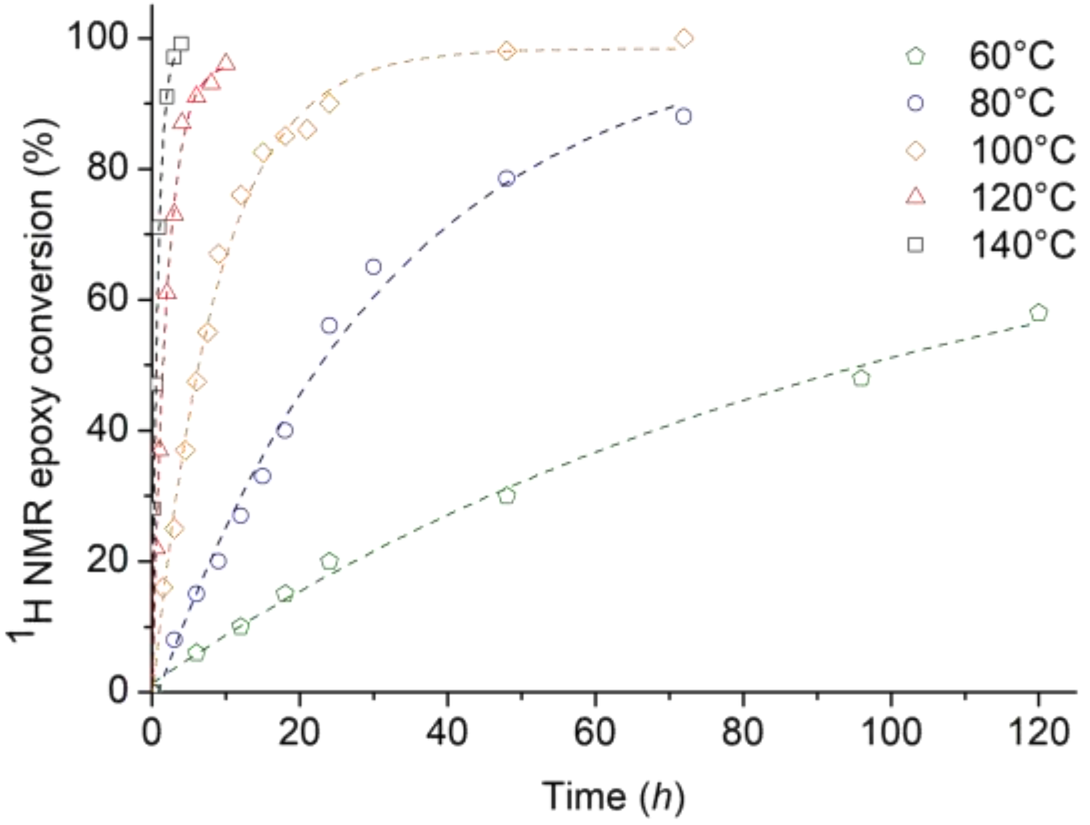
1- Find suitable conditions for material synthesis (T°C & water content)
2- Determine the mechanism (epoxy-acid addition and transesterification)
3- Is the enzyme still « alive » ?
4- Can we produce vitrimer or vitrimer-like materials ?

Model molecular reactions: Effect of temperature on epoxy-addition



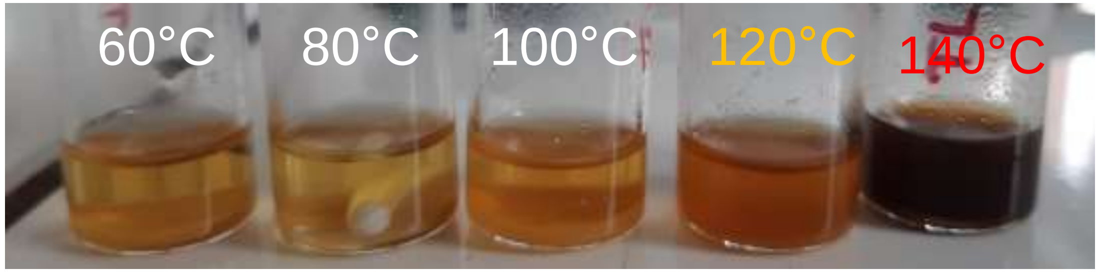
Label	Catalyst	T (°C)	Reaction time (in h)	^{1}H NMR conv. (%)
NC60	none	60	120	2
TL60	Lipase TL	60	120	50
NC80	none	80	72	5
TL80	Lipase TL	80	72	88
NC100	none	100	48 (72)	30 (50)
TL100	Lipase TL	100	48	98
NC120	none	120	10	32
TL120	Lipase TL	120	10	≥ 99
NC140	none	140	4	37
TL140	Lipase TL	140	4	≥ 99

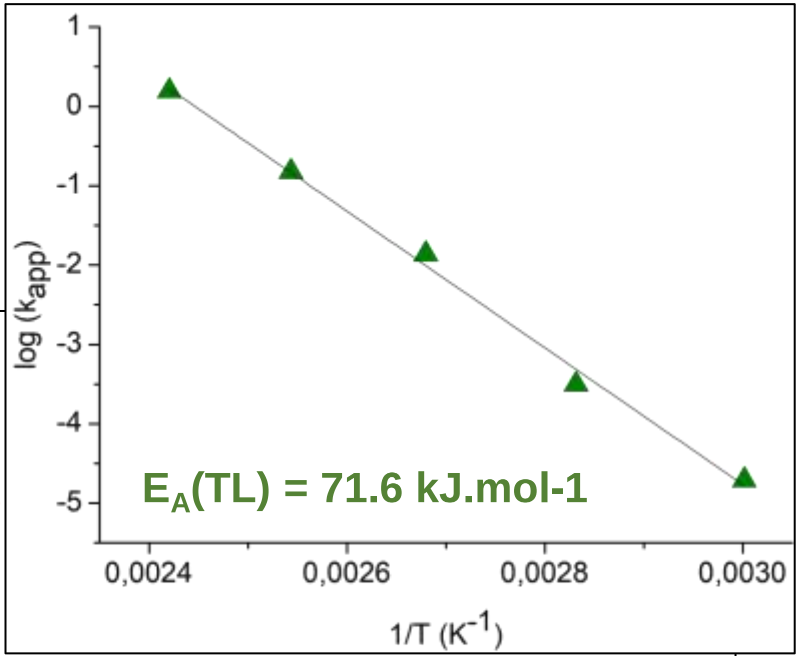
^{1}H NMR monitoring of epoxy consumption as a function of time

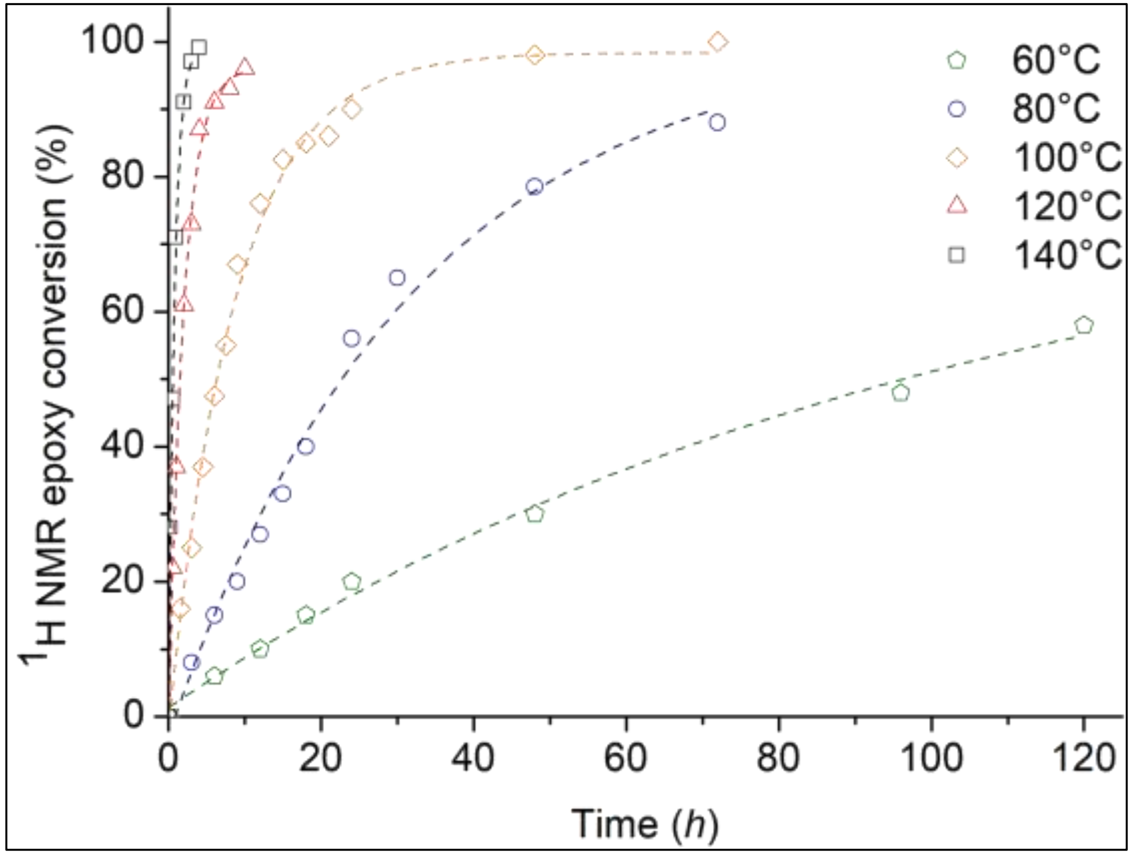


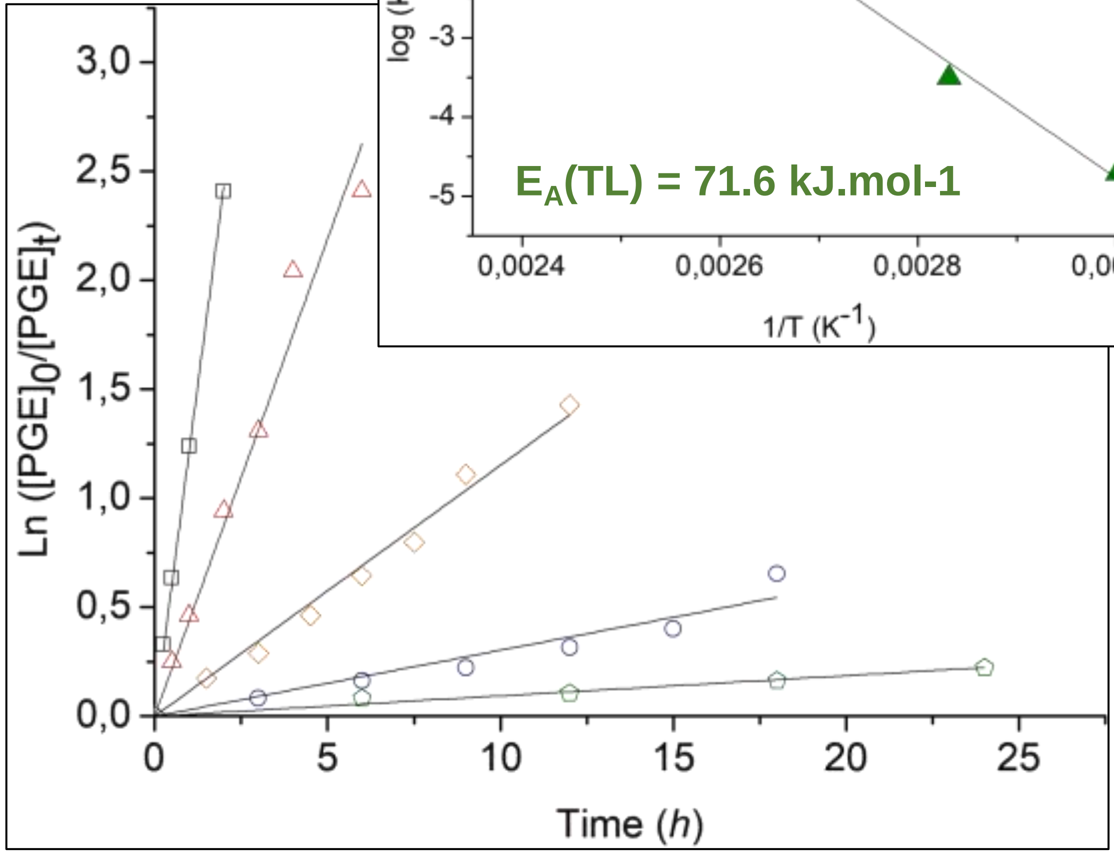
Biomacromolecules, **2021**, *22*, 4544-4551

Model molecular reactions: Effect of temperature on epoxy-acid addition









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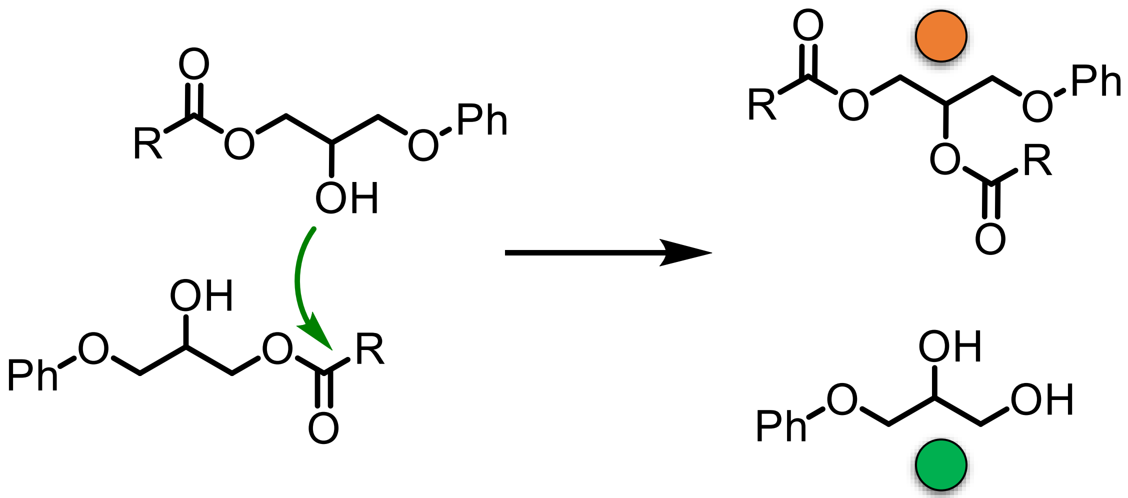
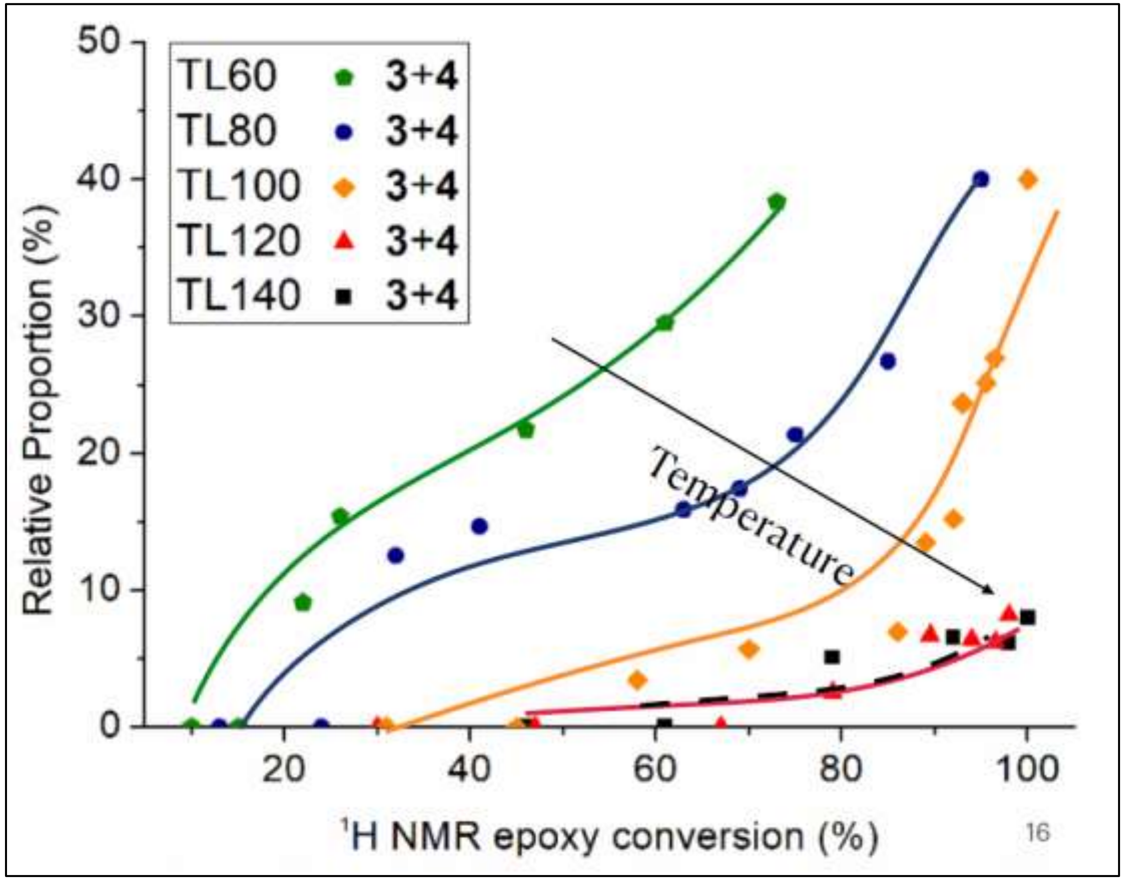
Model molecular reactions: Effect of temperature on transesterification





Transesterification only occured at temperature below 100°C

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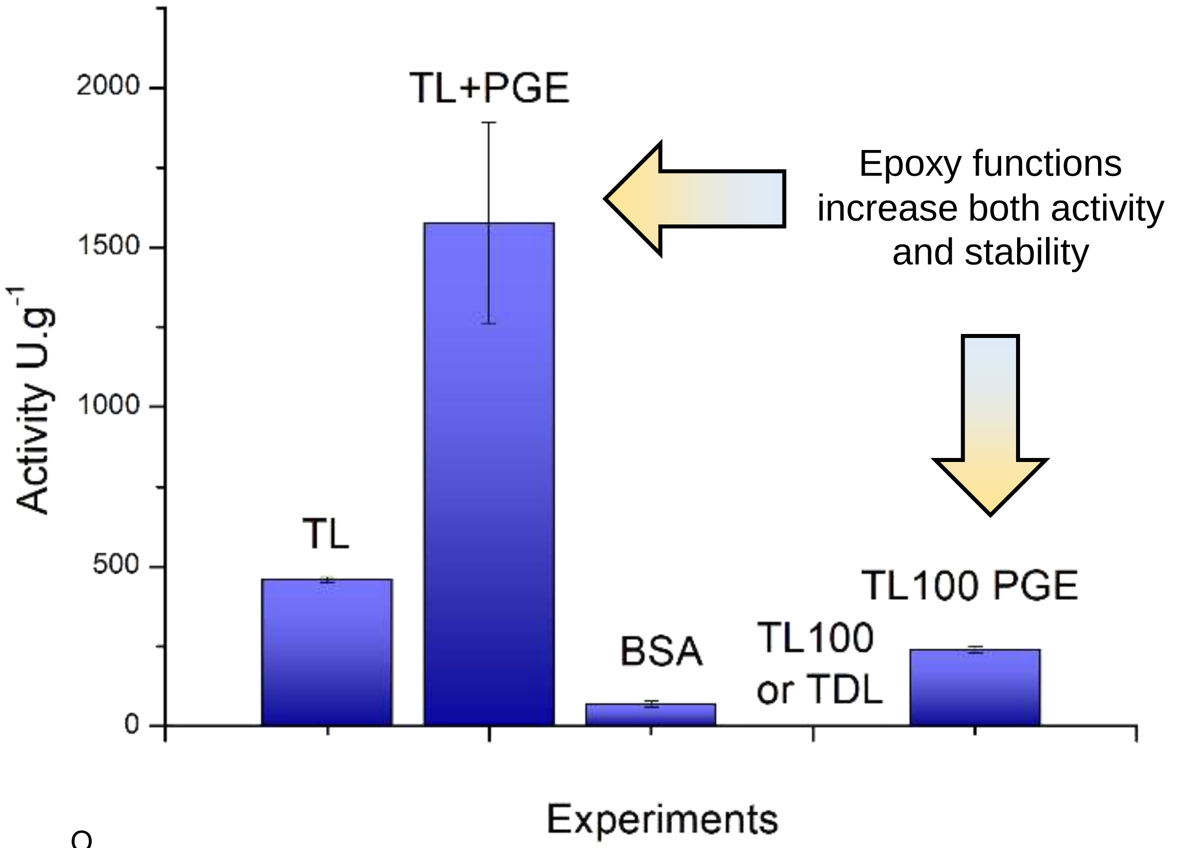
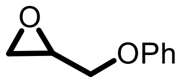
Model molecular reactions: Mechanistic investigation at 100°C

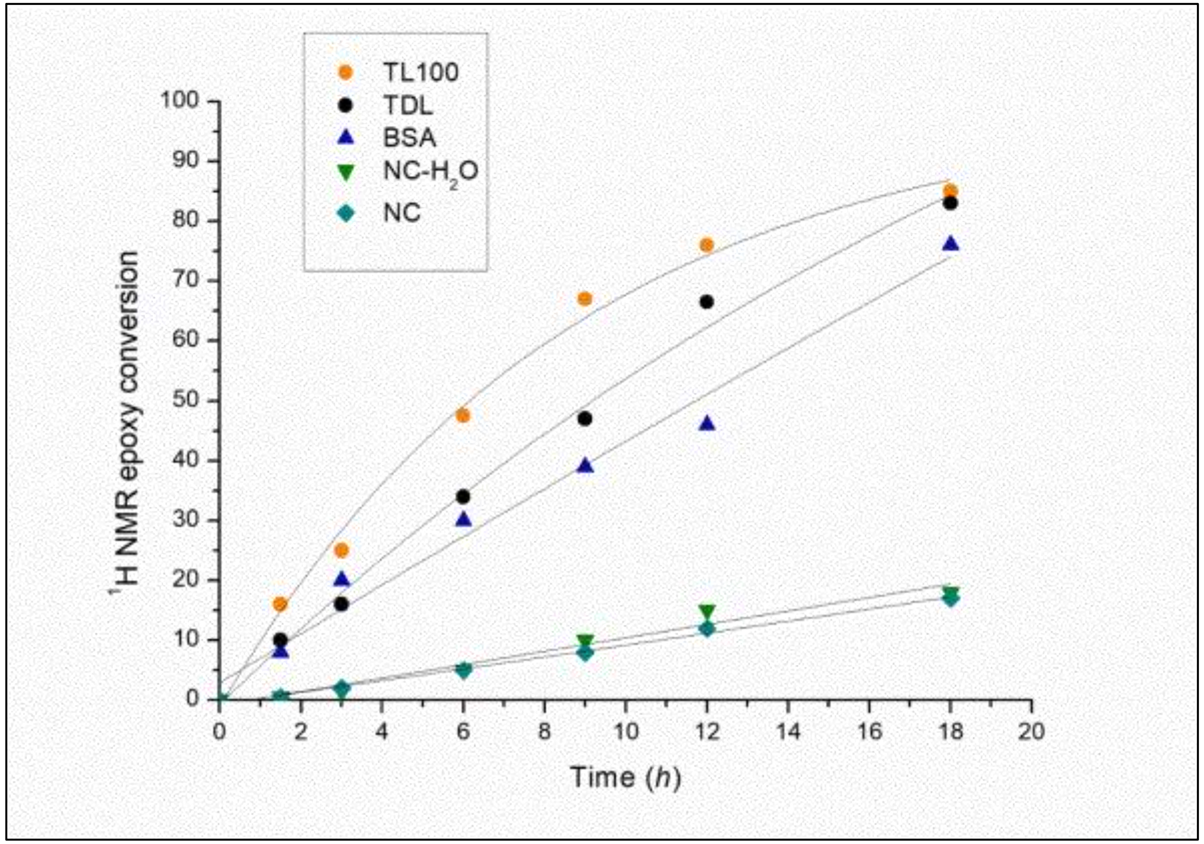
Enzymatic activity (titration of COOH from hydrolysis of triglycerides in emulsion at 50°C)





[PGE]

Kinetic experiments by ^{1}H NMR at 100°C with various enzymes



TL = Lipase TL
TDL = Thermally Denaturated Lipase (200°C, 3h)
BSA = Bovine Serum Albumin

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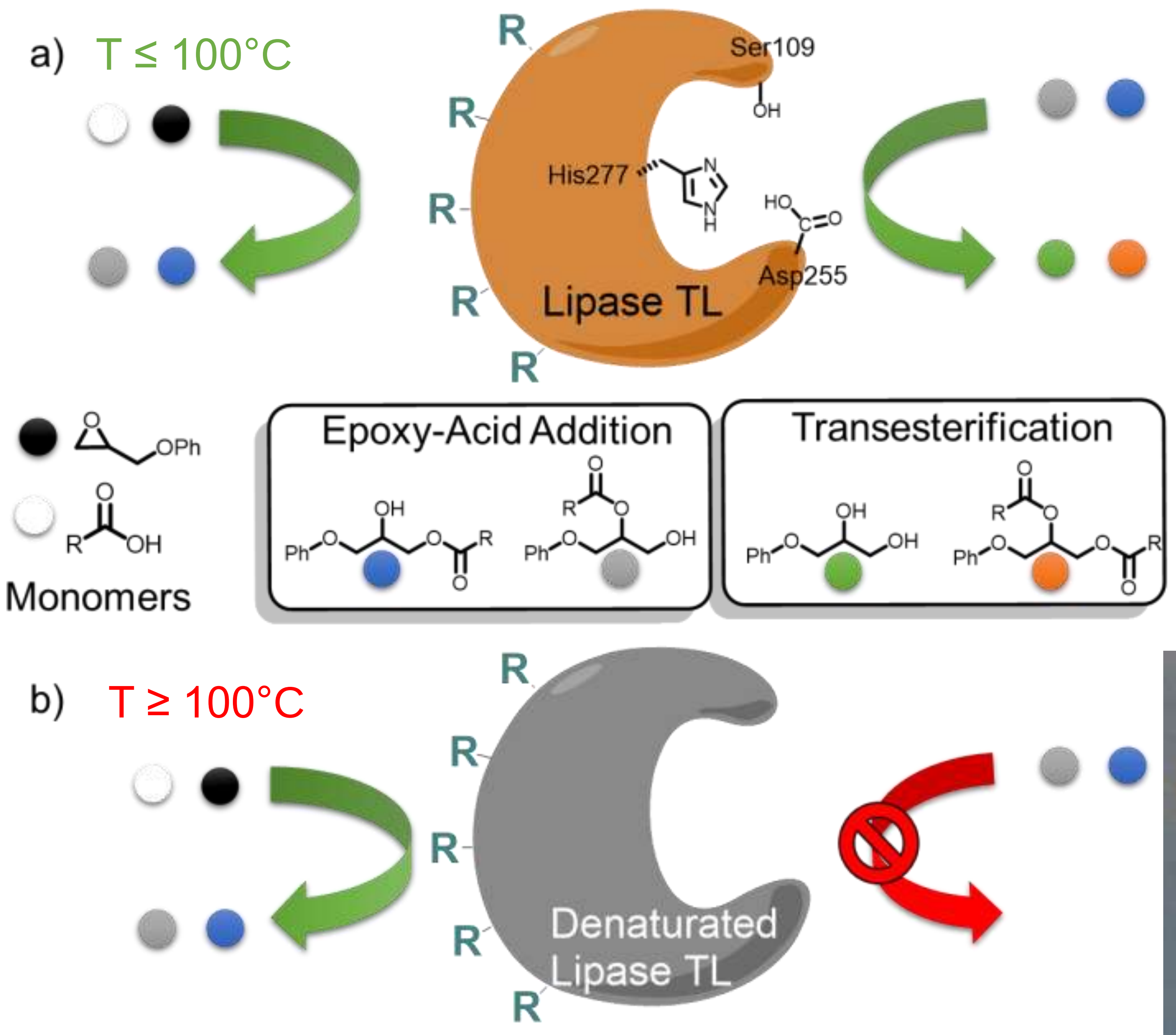
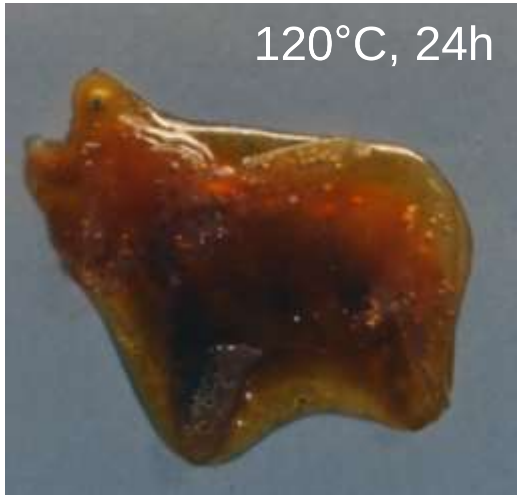
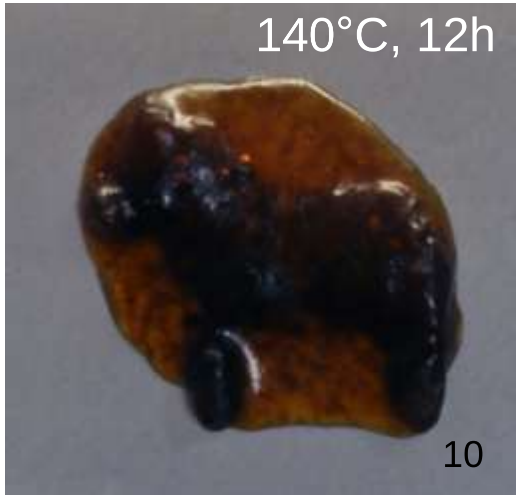
Model molecular reactions : Proposed mechanism

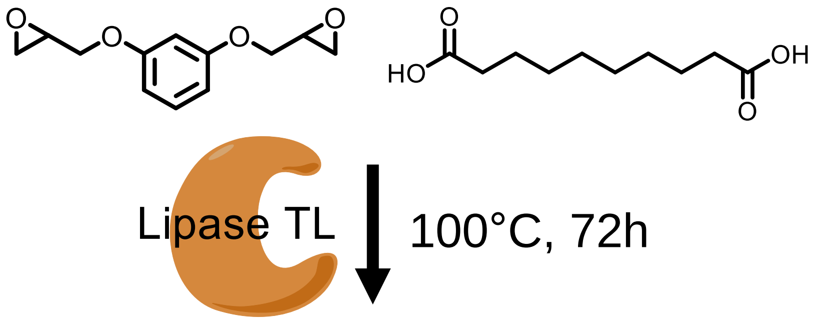


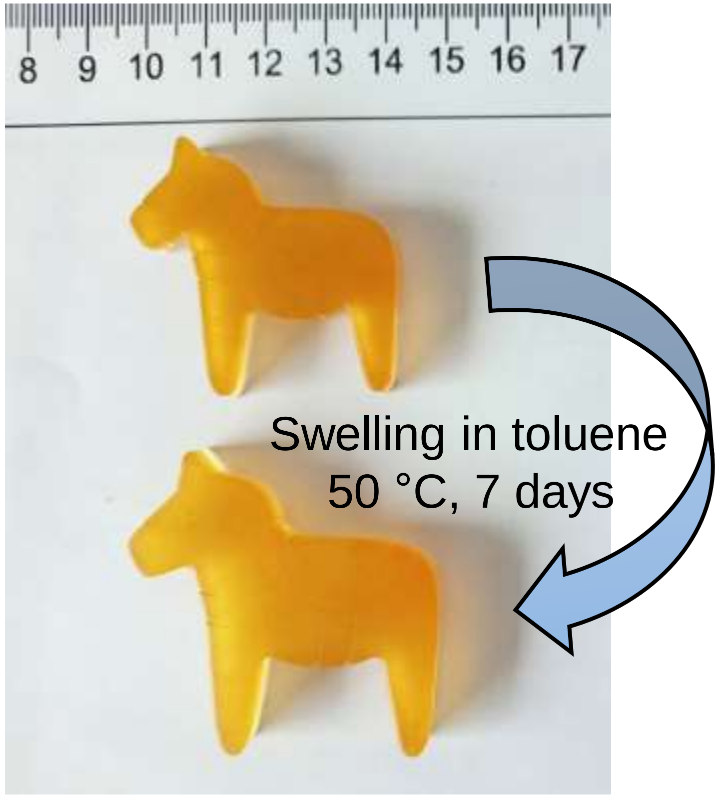




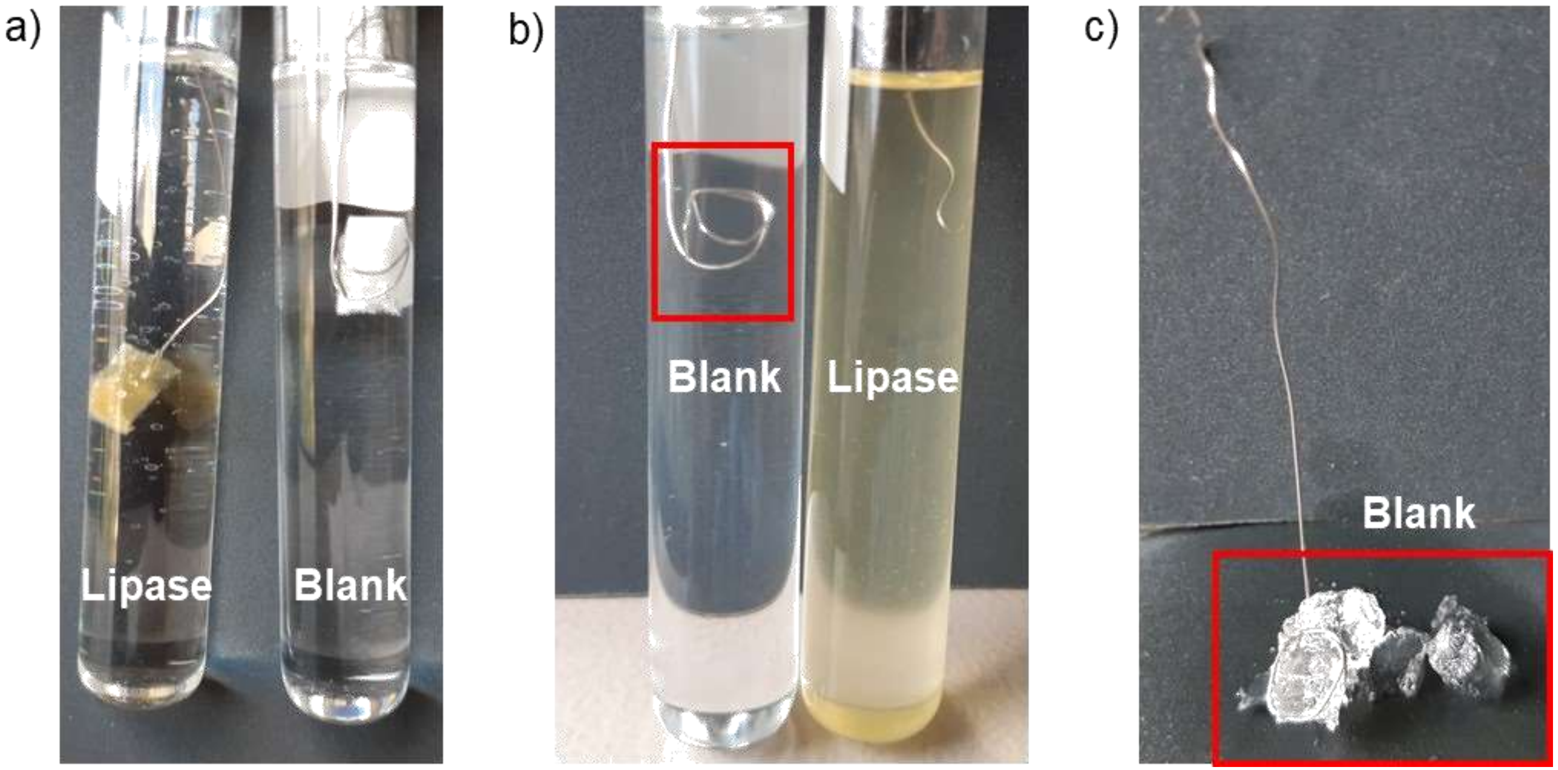
Biomacromolecules, **2021**, *22*, 4544-4551

Lipase catalysed polymerisation: A prototype material





Dissolution test in benzyl alcohol (100°C, 3 days)

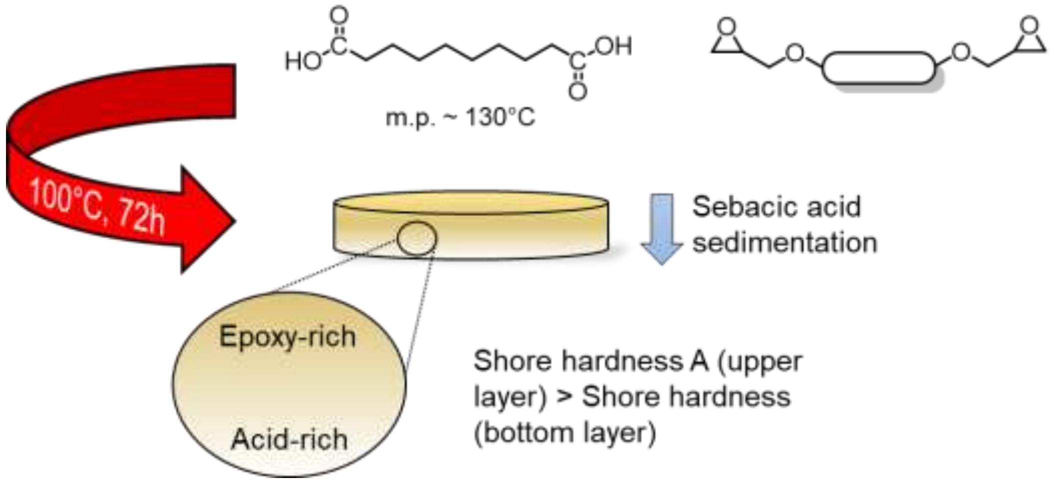


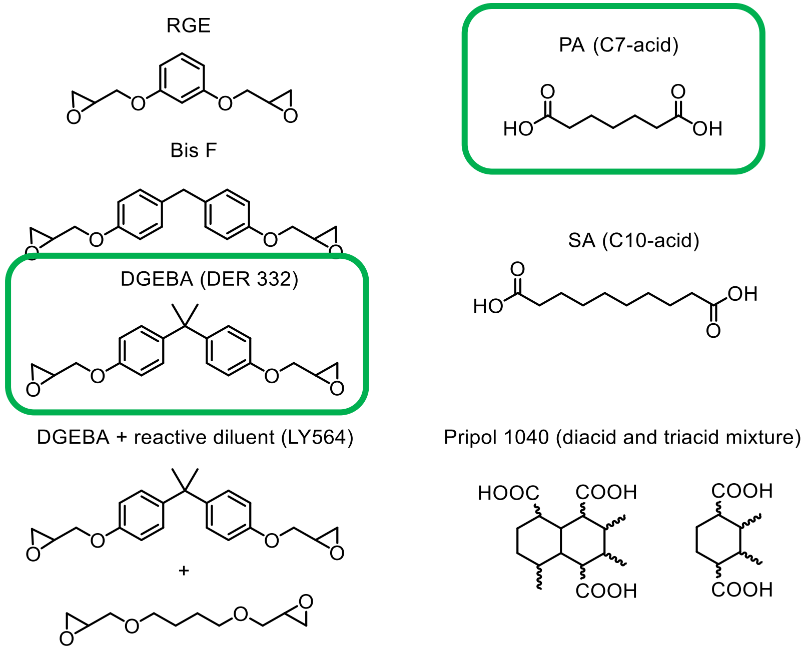
blank = control material synthesized without lipase

Extracted enzyme from model resin (not crosslinked) : A ≈ 270 $U.g^{-1}$

ACS Macro Lett. **2023**, *12*, 3, 338−343

Lipase catalysed polymerisation: looking for suitable formulation





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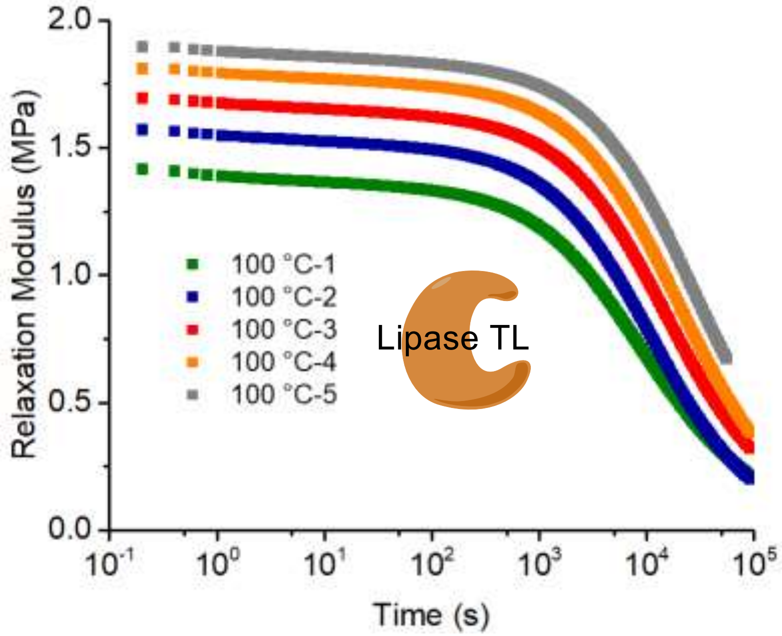
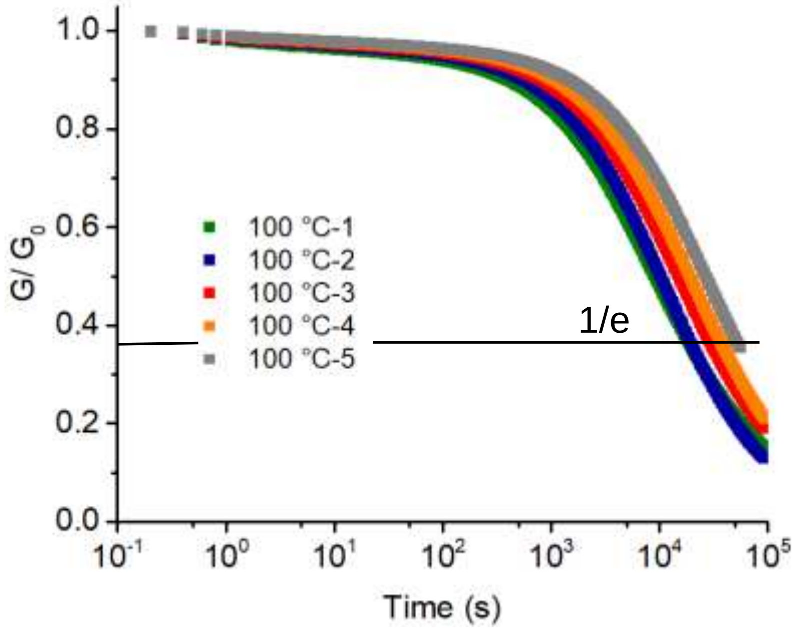
Lipase catalysed polymerisation: vitrimer properties

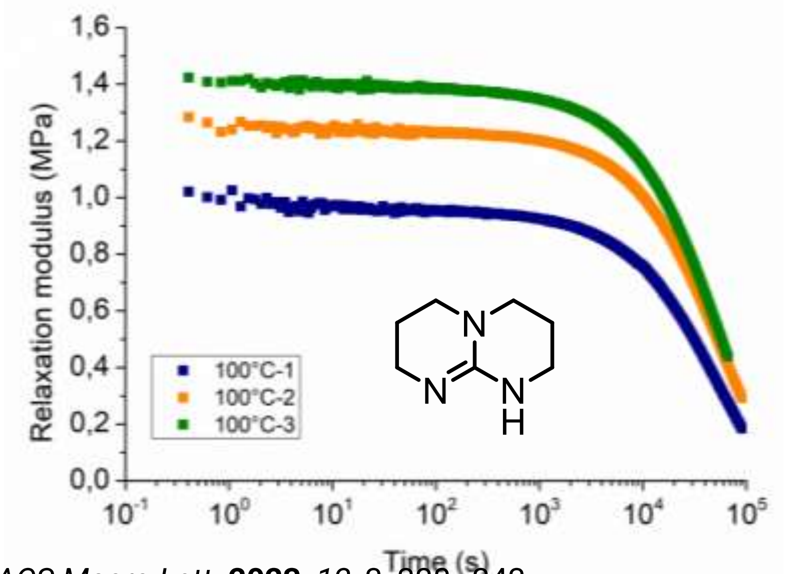


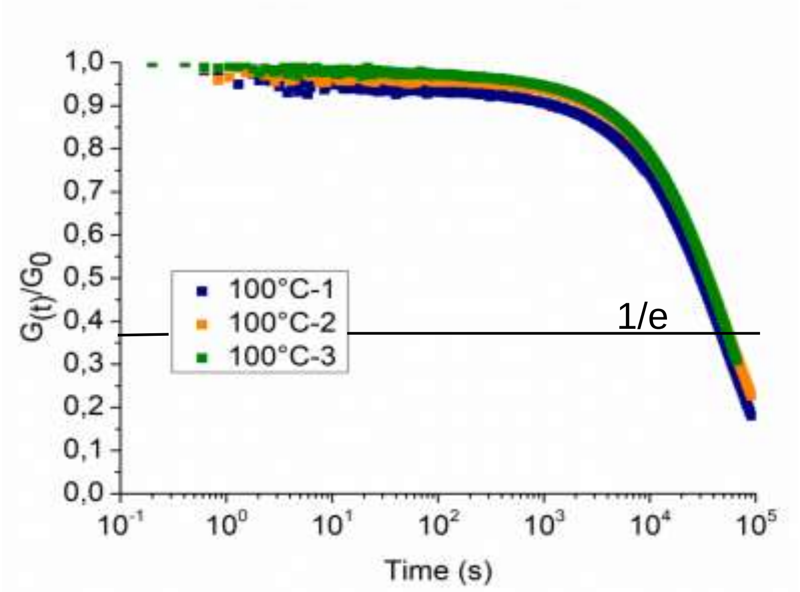
Stress relaxation (torsion, γ=0.5%) at 100°C



Normalised stress relaxation (torsion, γ=0.5%) at 100°C

- G_0 increases after each experiments (100°C, 24h)
- $\tau_{(1/e)}$ increases from ~ 4 h to ~ 18 h after 5 days at 100°C



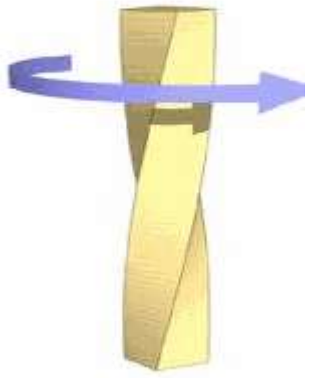


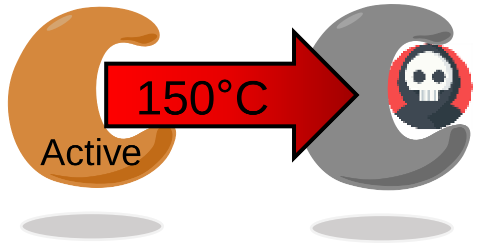
- Similar G_0 increase after each experiments for TBD catalysed material (100°C, 24h)
- $\tau_{(1/e)}$ is stable (~ 18 h)

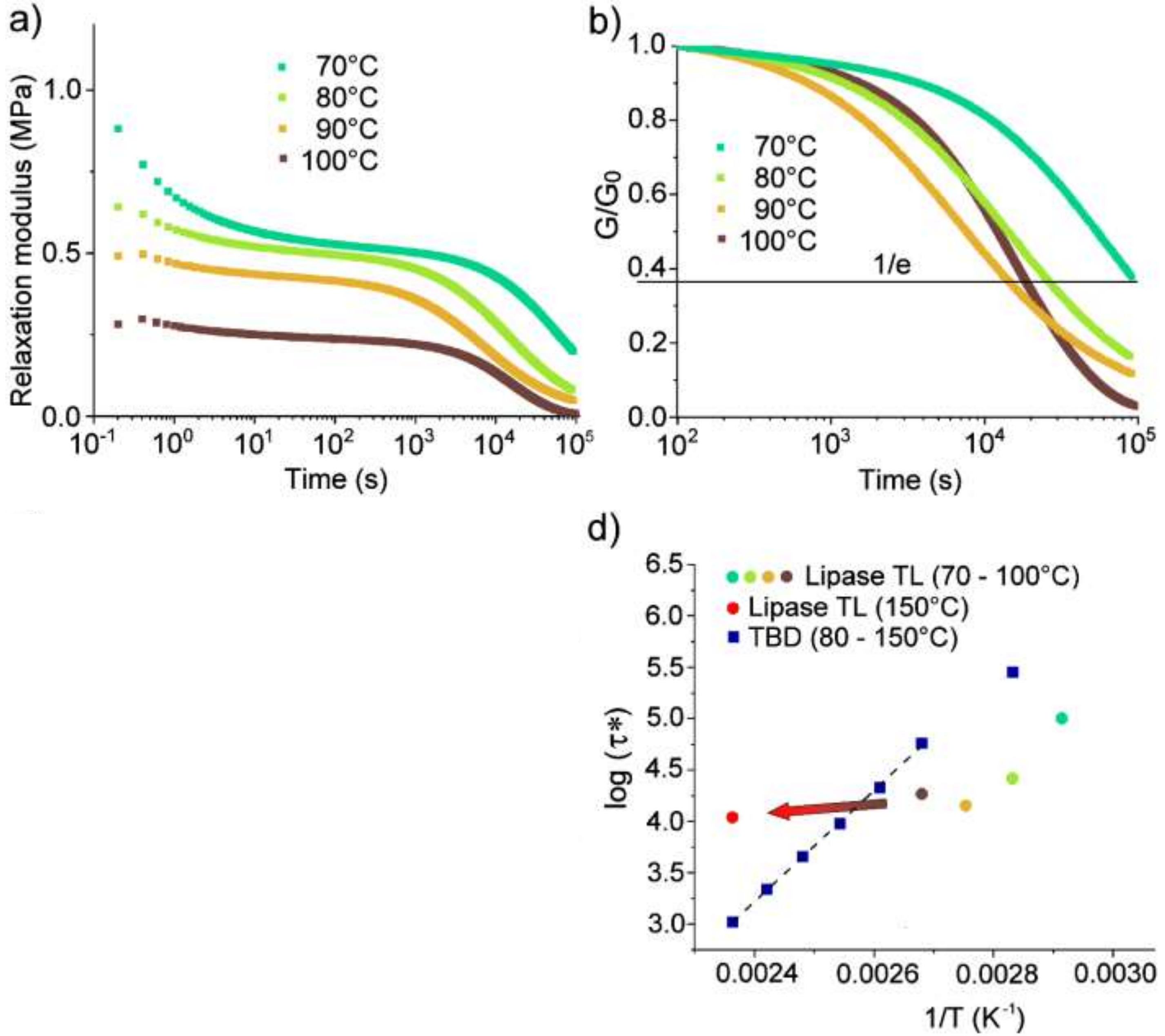
enzyme denaturation ??

ACS Macro Lett. **2023**, *12*, 3, 338–343

Lipase catalysed polymerisation: vitrimer properties







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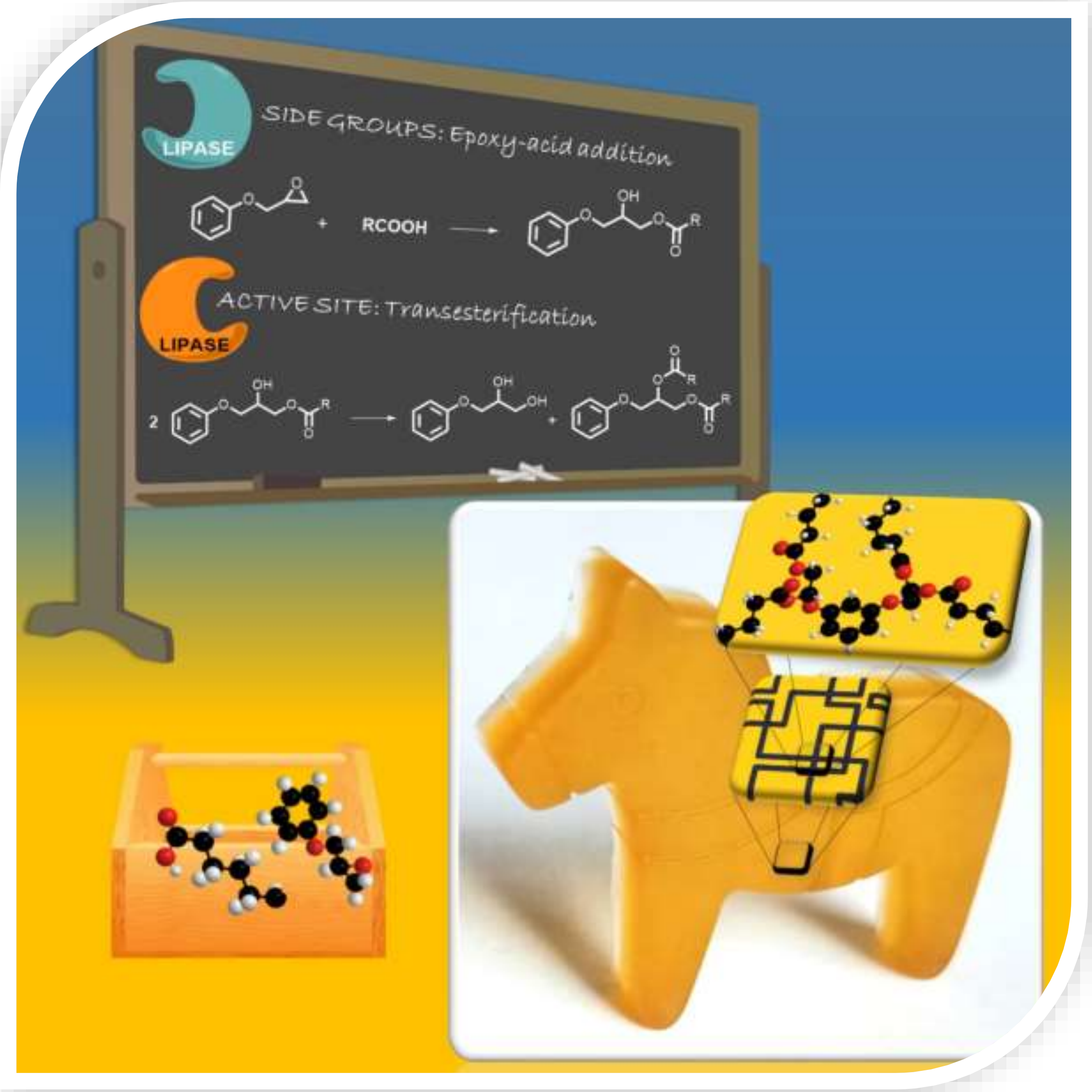
Conclusion



Molecular Model reactions

- ✓ Suitable conditions for Lipase catalysed epoxy-acid networks
- ✓ Mechanism insight (active site or side groups)

Vitrimer synthesis

- ✓ Suitable formulations for Lipase catalysed epoxy- acid networks
- ✓ Able to relax stress and reprocess multiple times at 100°C
- ✓ Lipase catalyses the exchange reactions

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Self-**HE**aling soft **RO**botics

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