

ADMET polymers from D-xylose and castor oil†



UNIVERSITY OF
BATH



Centre for **Sustainable
& Circular** Technologies

Marco Piccini, Dr Antoine Buchard

Centre for Sustainable and Circular Technologies, University of Bath, BA2 7AY, UK

✉ m.piccini@bath.ac.uk

www.csct.ac.uk

🐦 @Marco_Piccini



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Bio-based monomers and polymers

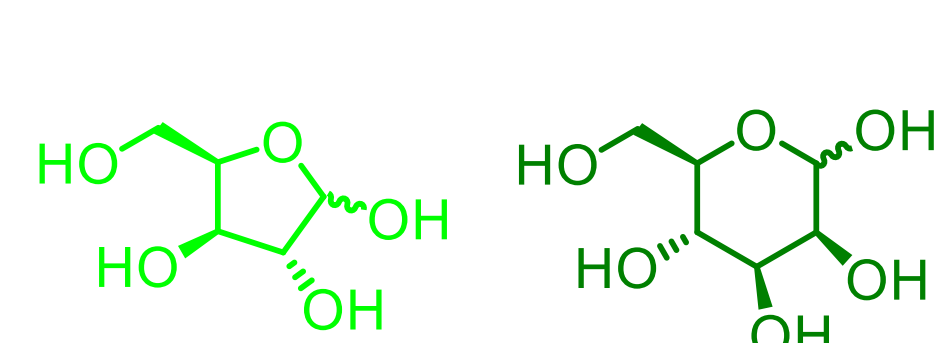
- ◆ **Fossil-derived plastics** create a number of **issues**, i.e. environmental pollution, resource depletion and global warming
- ◆ Research towards **bio-based** and **(bio)degradable** polymers is of utmost importance
- ◆ **Carbohydrates** are the **most attractive feedstock** for renewable monomers and polymers thanks to their abundance, low cost, extensive structural and stereochemical diversity, hydrophilicity, hydrolytic degradability and nontoxicity
- ◆ **Sugars** have been used for the production of **many monomers** through different routes,¹ mainly **fermentation** (e.g. lactic acid), **oxidation/reduction** (e.g. isosorbide), **dehydration** (e.g. furans) or **without structural modification** (few examples)
- ◆ Recently, **olefin metathesis** has been applied to the polymerisation of sugar-derived monomers, particularly **acyclic diene metathesis (ADMET) polymerisation**²



Aims

- Synthesis of polymers containing **sugar cores with unmodified backbone**
- Use of **sugars from 2nd generation feedstocks** → xylose and mannose
- Incorporating **flexible chains** (fatty acids) to overcome polymer brittleness
- Exploitation of olefin metathesis chemistry, in particular **ADMET polymerisation**

Materials



♣ **Xylose**, a pentose sugar, is the mayor component of **hemicellulose**, which are abundant, easily hydrolysed and potentially sourced from wastes (e.g. agricultural waste) → second generation feedstock

♣ **Mannose**, an hexose, is also present in hemicelluloses in significant amount

♣ **10-Undecenoic acid** is also renewable, derived from castor oil (a plant oil) through cracking of ricinoleic acid

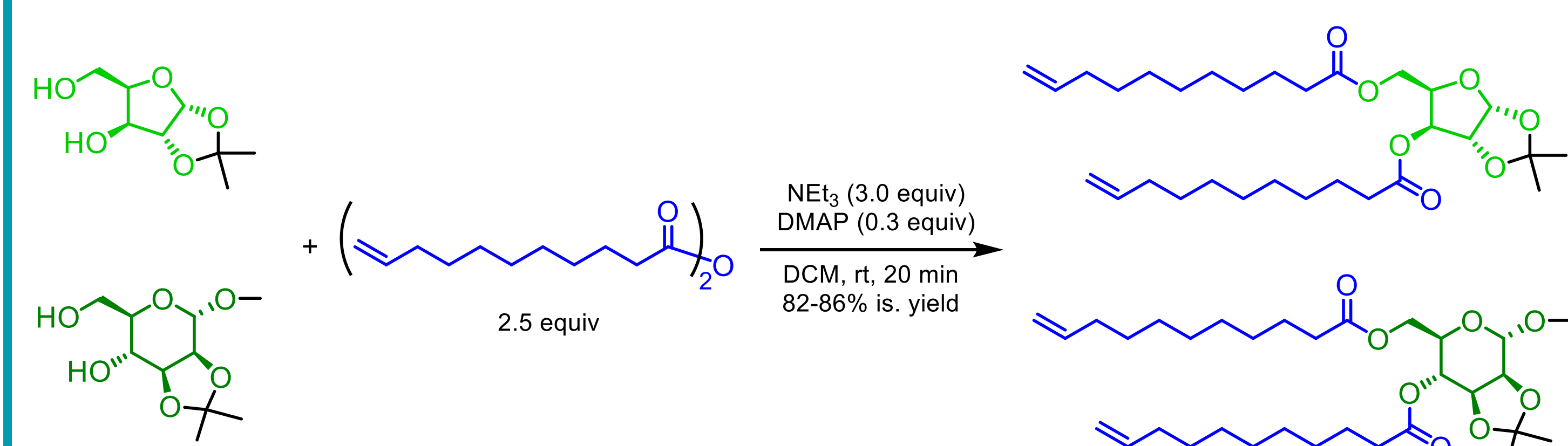
References

1. Gandini et al., *Macromolecules* **2008**, *41*, 9491; *Green Chem.* **2011**, *13*, 1061; *Prog. Polym. Sci.* **2015**, *48*, 1
2. (a) Fokou, Meier, *J. Am. Chem. Soc.* **2009**, *131*, 1664; (b) Shearouse, Lillie, Reineke, Tolman, *ACS Macro Lett.* **2015**, *4*, 284; (c) Lillie, Tolman, Reineke, *Polym. Chem.* **2017**, *8*, 3746; (d) Hibert, Grau, Pintori, Lecommandoux, Cramail, *Polym. Chem.* **2017**, *8*, 3731

Monomer synthesis

🎵 **Protection of sugars:** sugar diols were obtained *via* a simple one pot, two step reaction (double protection followed by selective hydrolysis): from D-xylose with acetone/H⁺, from methyl α-D-mannopyranoside with 2,2-dimethoxypropane/H⁺ (70-90% yields on 20 g scale, no purification required apart from extraction)

🎵 **Double esterification** of sugar diols with 10-undecenoic anhydride:

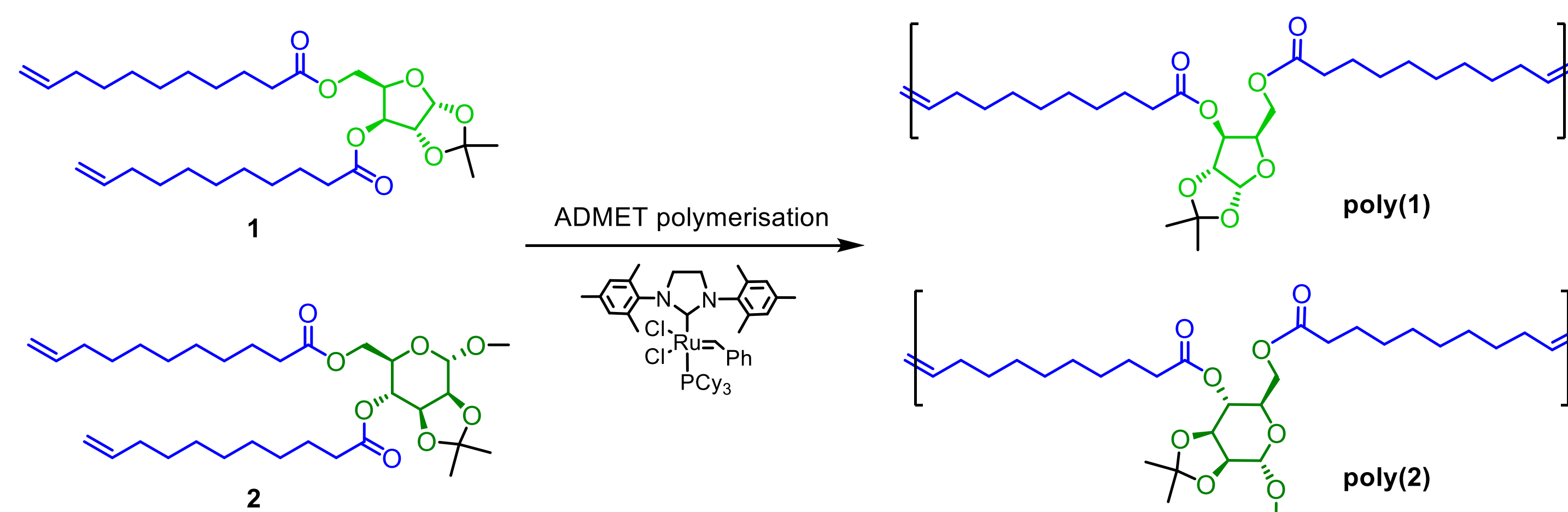


ADMET polymerisation

- ☀ **ADMET polymerisation** of α,ω-diene monomers was conducted in bulk under dynamic vacuum with commercial Grubbs 2nd gen. catalyst
- ☀ **1 and 2** were polymerised under **different conditions**, studying the effect of temperature (20 - 90 °C), catalyst loading (0.1 - 4.0 mol%), presence of solvents, mixing technique (magnetic/mechanical stirring)
- ☀ **High molecular weights** were obtained (M_n up to 71 kg mol⁻¹) using **low catalyst loadings** (0.5 - 0.1 mol%); **mechanical stirring** was key to obtain high M_n , overcoming mass transfer limitations from viscosity

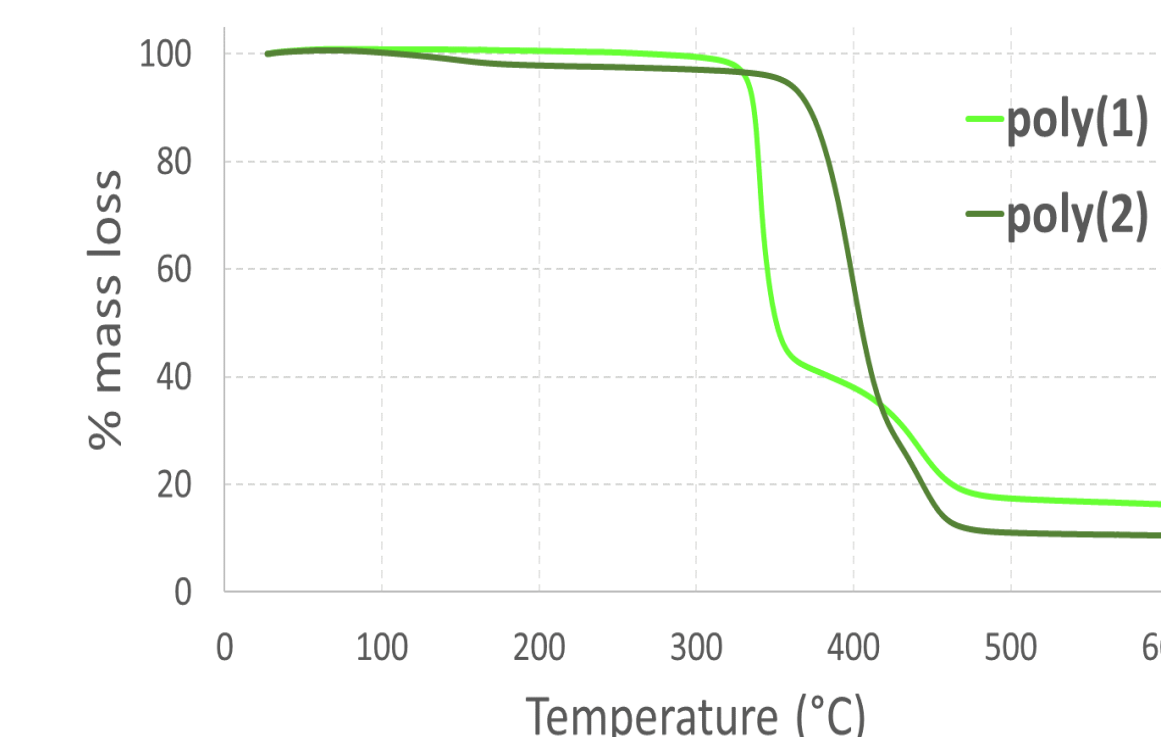
Key results	#	Monomer	Catalyst [mol%]	Mixing	Yield [%]	M_n^a [g mol ⁻¹]	$\bar{D}^a$
	1	1 (xylose)	0.5	Magnetic	84	20,600	1.8
	2	1 (xylose)	0.5	Mechanical	70	71,400	2.1
	3	1 (xylose)	0.1	Mechanical	82	68,200	2.4
	4	2 (mannose)	1.0	Magnetic	91	49,500	2.3
	5	2 (mannose)	0.1	Mechanical	83	60,800	3.5

Conditions: Grubbs 2nd gen. cat., bulk, 90 °C, 0.1 mbar, 20 hours; conversion 100%. ^a Estimated by GPC in THF vs polystyrene standards (RID)

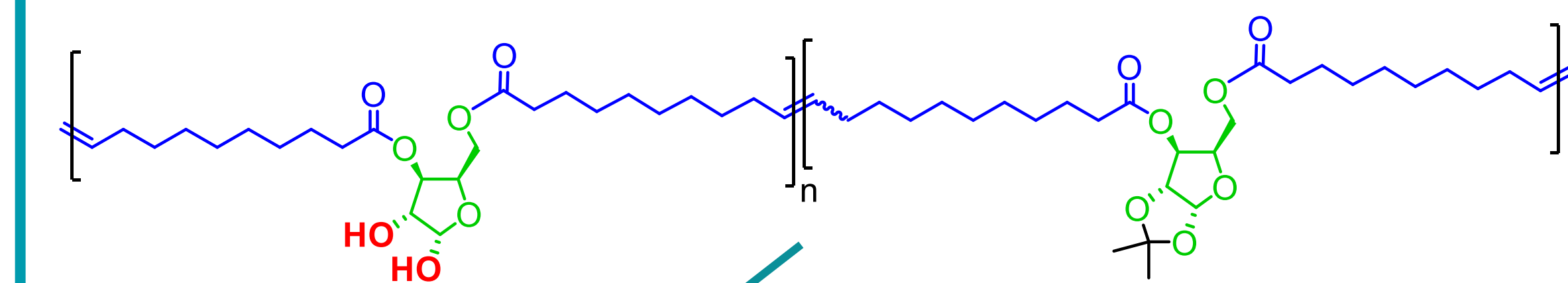


Properties

- ☼ **Highly thermally stable** polymers ($T_{d5\%}$ 330-355 °C), showing two distinct decomposition steps
- ☼ **Low glass transition** temperatures (T_g -28 – -8 °C), as expected, due to the flexible fatty acid chains; polymers are **amorphous rubbery materials**
- ☼ Stable to hydrolysis (pH = 0, 7, 14)



Post-modification & film casting



- ☼ Partial ketal **deprotection** changed the polymer properties, imparting a **semicrystalline** behaviour (T_m ~50 °C) and preventing solubilisation in common solvents
- ☼ This allowed to produce flexible transparent **polymer films** by solvent casting

- ☼ **Mechanical properties** typical of rubbers
- ☼ **OH groups were functionalised** with Ph₂PCl, allowing post-polymerisation modification towards new functional materials

Conclusions

- ✓ Two **novel renewable polymers** were synthesised via ADMET polymerisation
- ✓ **High molecular weight** polymers were obtained (M_n up to 71 kg mol⁻¹) using **low catalyst loadings**
- ✓ Polymers were **amorphous rubbers** with high thermal and hydrolytic stability
- ✓ Partial ketal deprotection gave **semicrystalline** materials allowing production of **polymer films**
- ✓ **Post-polymerisation modification** of OH groups was possible