

**Biorenewable Polymers 1:
The Isotactic Polymerisation of Lactide**

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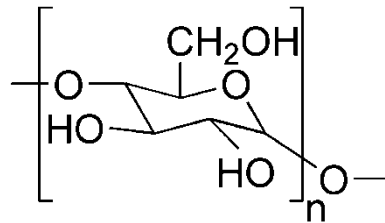
Over the next hour you should acquire the knowledge to:

- 1. Describe why the polymerisation of lactide is so intensely researched.**
- 2. Explain how chiral and achiral (salen)-supported Al complexes may be used to prepare isotactic and syndiotactic polylactide.**

PLA is biorenewable, biocompatible and bioresorbable – it is also readily degraded chemically for recycling, but it is not strictly biodegradable

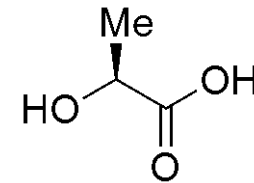


corn



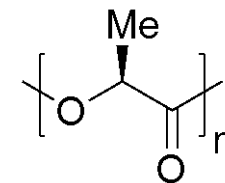
starch

fermentation



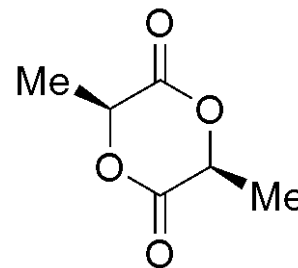
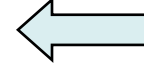
L-lactic acid

step-growth
condensation (-H₂O)



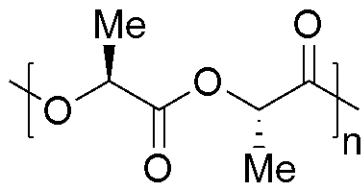
oligomers

heat



L-lactide

ring-opening
polymerisation
(chain growth)

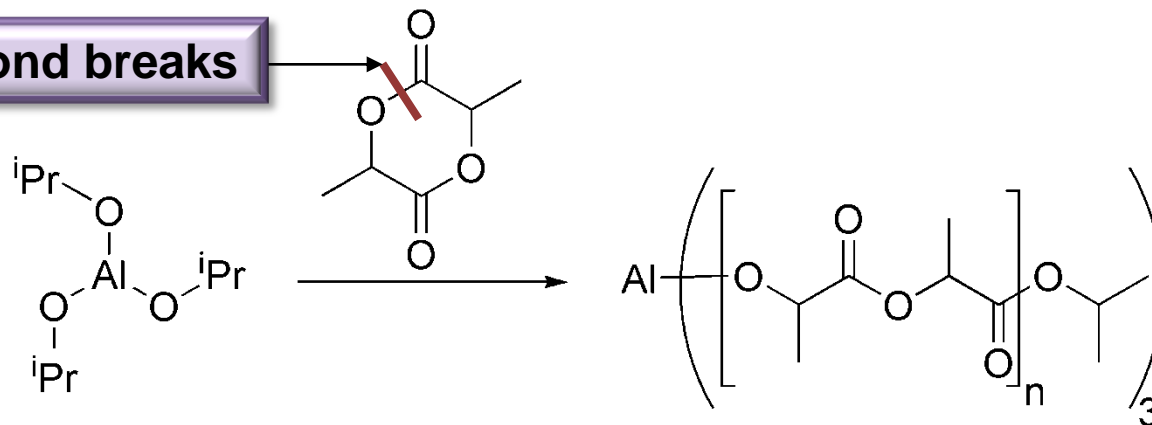


Poly(L-lactic acid), PLLA

We will focus on this step

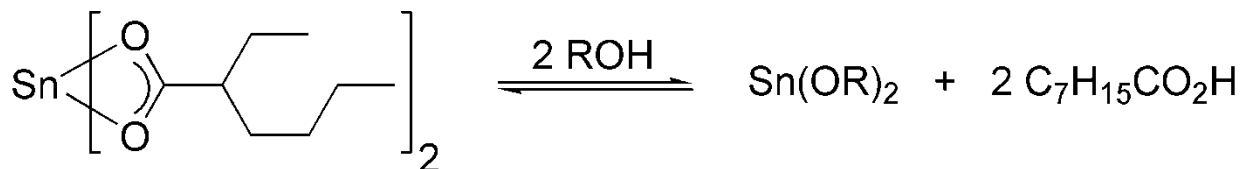
Typical initiators for lactide polymerisation are metal-alkoxides, e.g. $\text{Al}(\text{O}^i\text{Pr})_3$:

Acyl-oxygen bond breaks



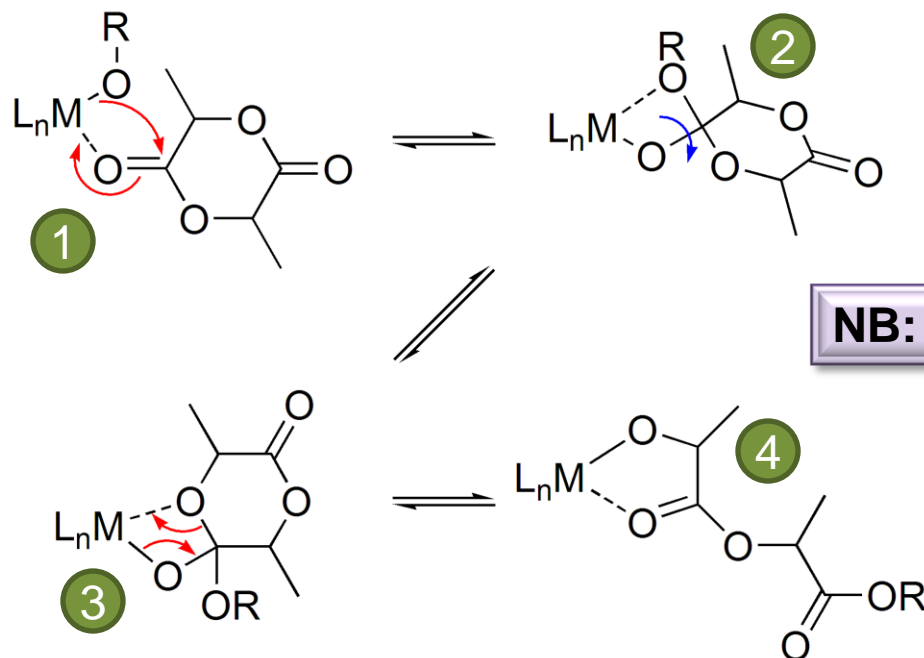
Metals used: Al, Mg, Zn, Fe, Y, Ti, Zr, Sn, Ca, La, Sm + others

Industrially, the initiator used is a tin(II) carboxylate - in the presence of alcohol, this is believed to form tin(II) alkoxides:



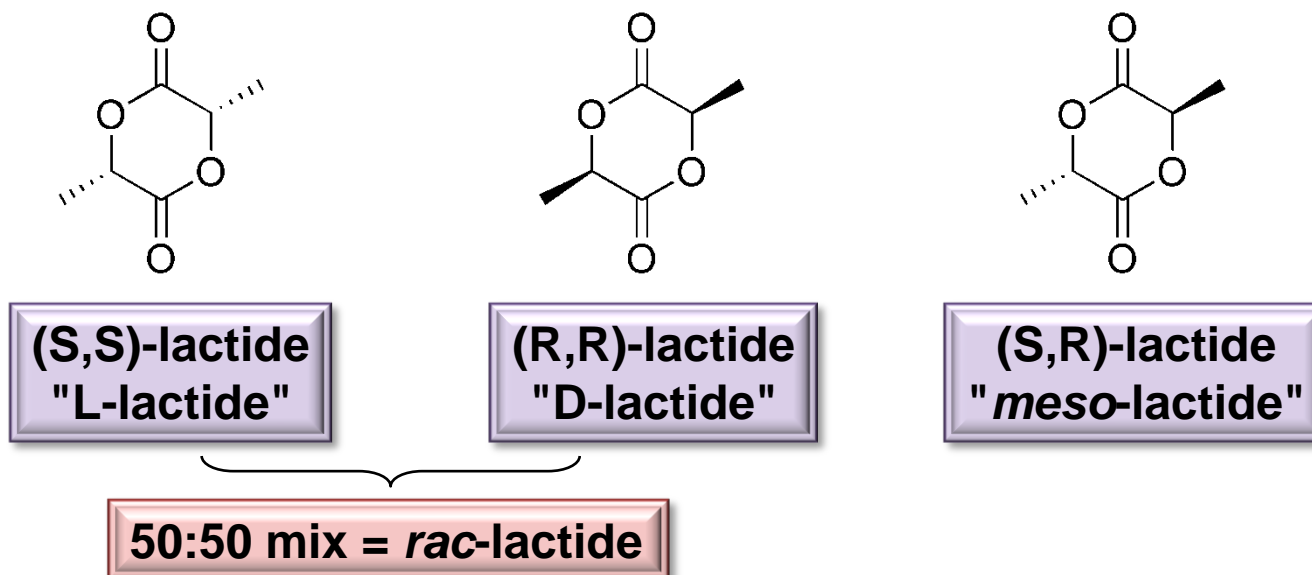
tin(II) bis(2-ethylhexanoate), "SnOct₂"

“Coordinative-Insertion Mechanism” - other lactones open in a similar way



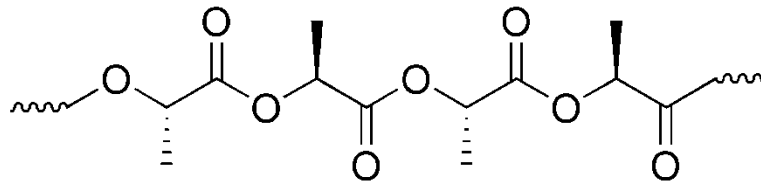
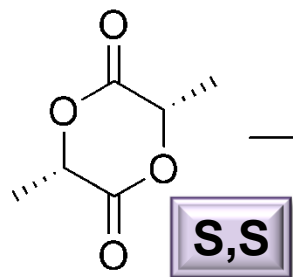
NB: Every step is reversible

1 Initiation involves nucleophilic attack of the alkoxide at the lactide carbonyl. This leaves the monomer heterocycle intact **2**. In order to open the ring, the monomer rolls around **2** → **3** to place the acyl oxygen nearer the metal centre **3**. This results in another metal alkoxide **4**, which can now insert the next monomer unit.

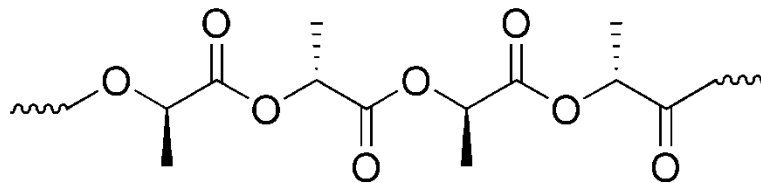
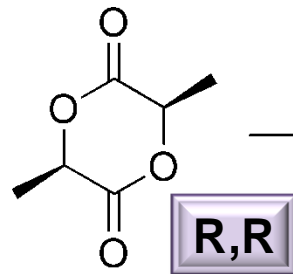


Since L-lactic acid is the naturally occurring form, (S,S)-lactide is much cheaper than (R,R)-lactide. *Meso*-lactide is not commercially available and must be separated from the (R,R) and (S,S) monomers by a steam distillation.

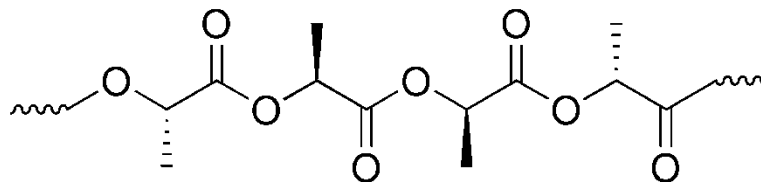
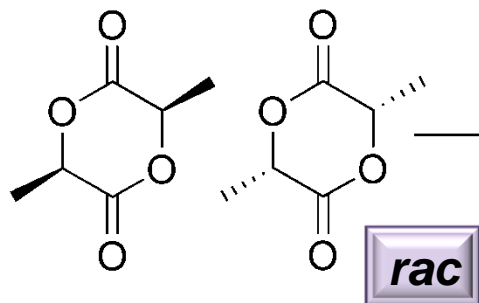
Most commonly studied: L-lactide and *rac*-lactide



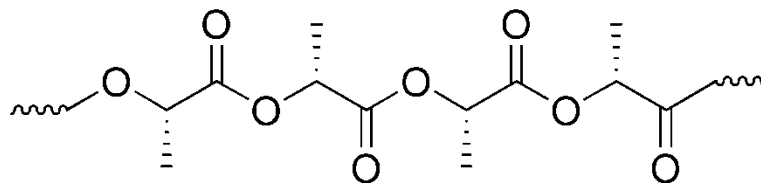
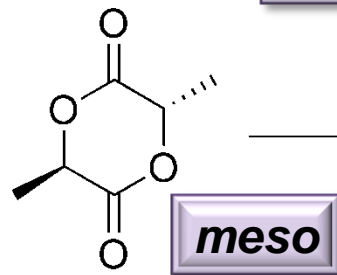
isotactic
-(SSSSSSSS)-
"poly(L-lactide)"



isotactic
-(RRRRRRRR)-
"poly(D-lactide)"



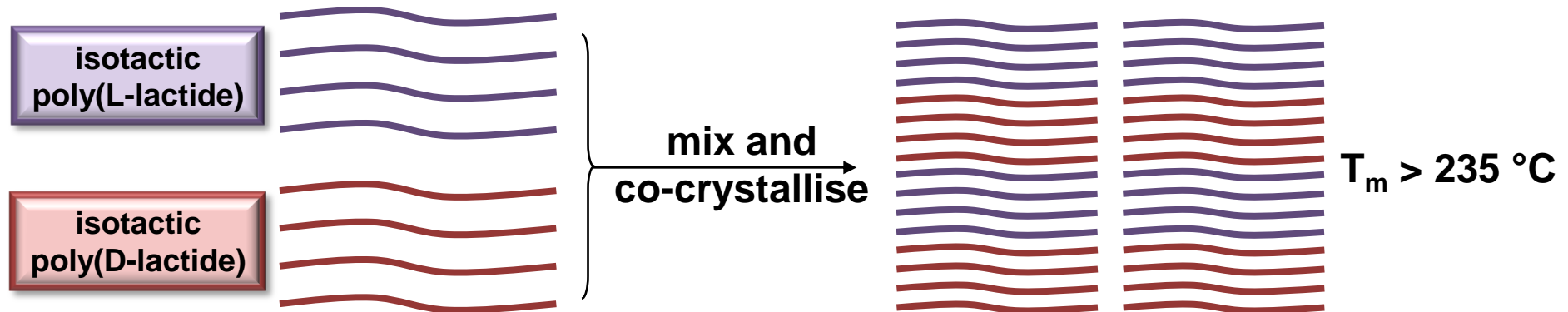
heterotactic
-(SSRRSSRR)-



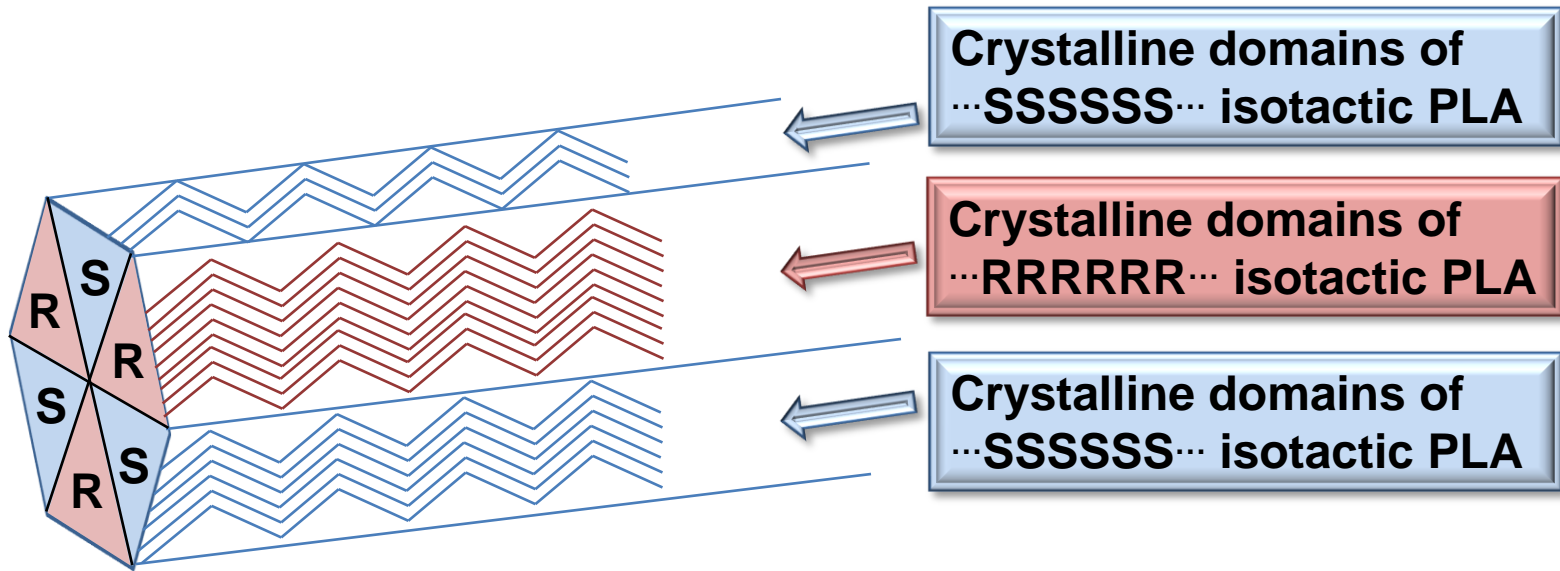
syndiotactic
-(SRSRSRSR)-

Polymer	T_m (°C)	T_g (°C)	Modulus (GPa)	Degradation time (months)
isotactic PLA	170	60	2.7	>24
syndiotactic PLA	153	45	n/a	n/a
heterotactic PLA	amorphous	49	n/a	n/a
atactic PLA	amorphous	55	1.9	12 - 16

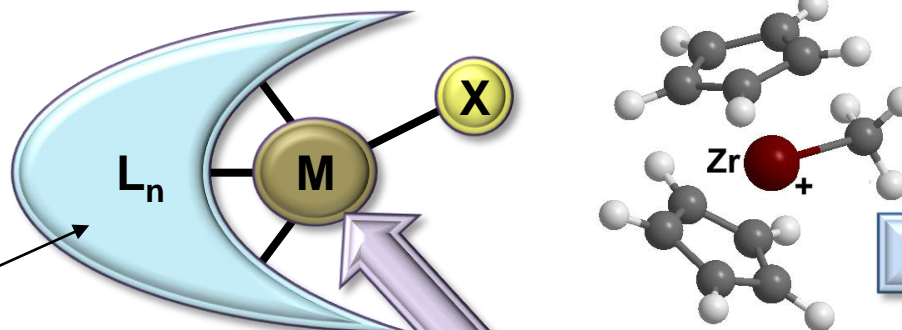
There is one other important form of PLA known as an isotactic stereocomplex:



Hexagonal prismatic crystals:



Additional crystallinity arises from the interfaces between the trigonal prisms of all S and all R PLA



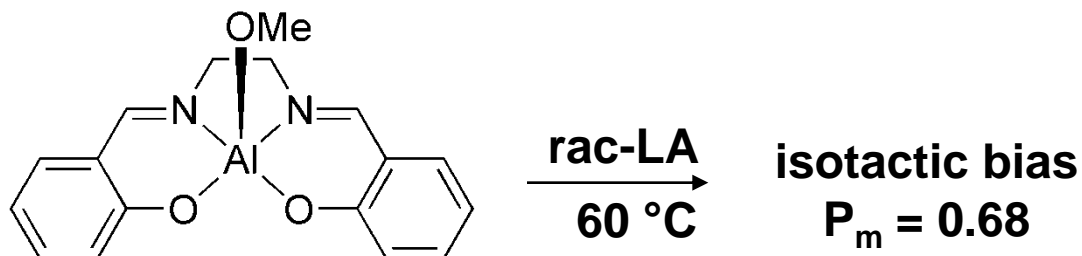
e.g. $[\text{Cp}_2\text{ZrMe}]^+$

sterically bulky
ancillary ligand(s)

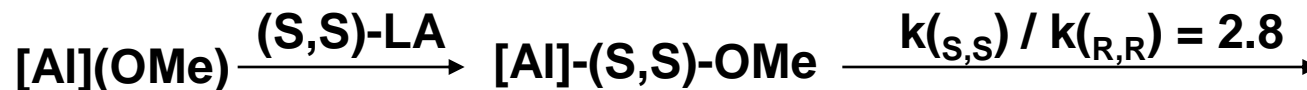
substrate approaches
vacant coordination site
and may then react with X

Polymer stereochemistry can potentially be
controlled by the sterics / chirality of L_n

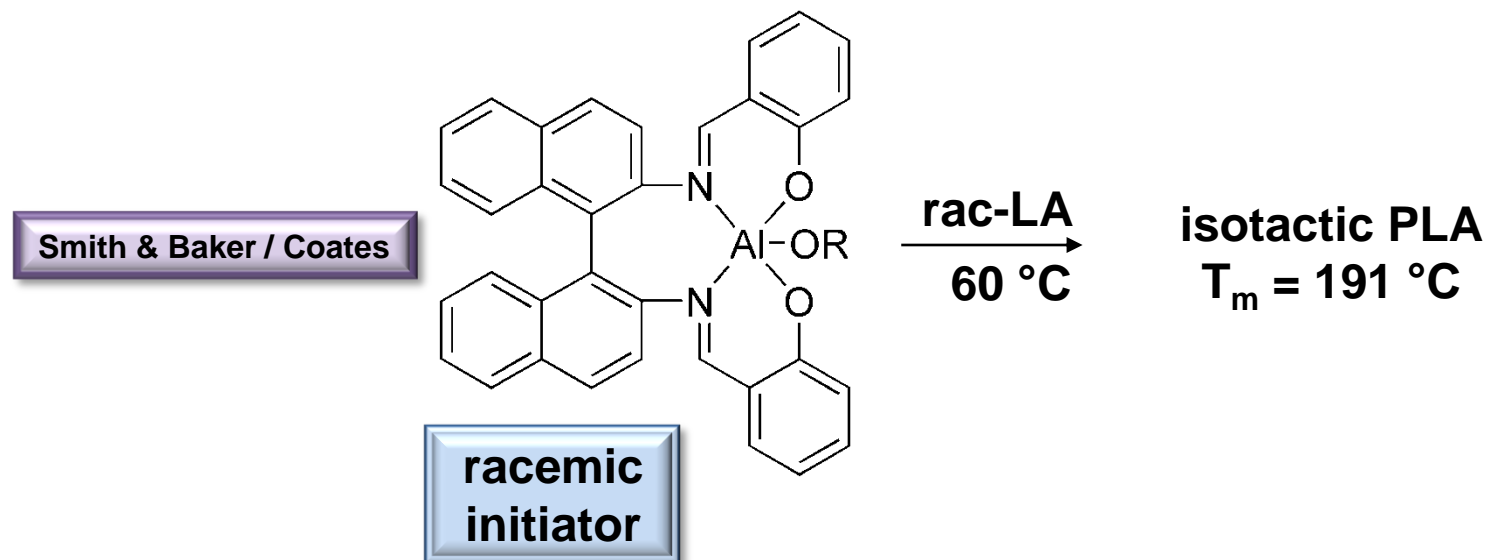
Spassky



Stereoselectivity presumably arises from a chain-end control mechanism:



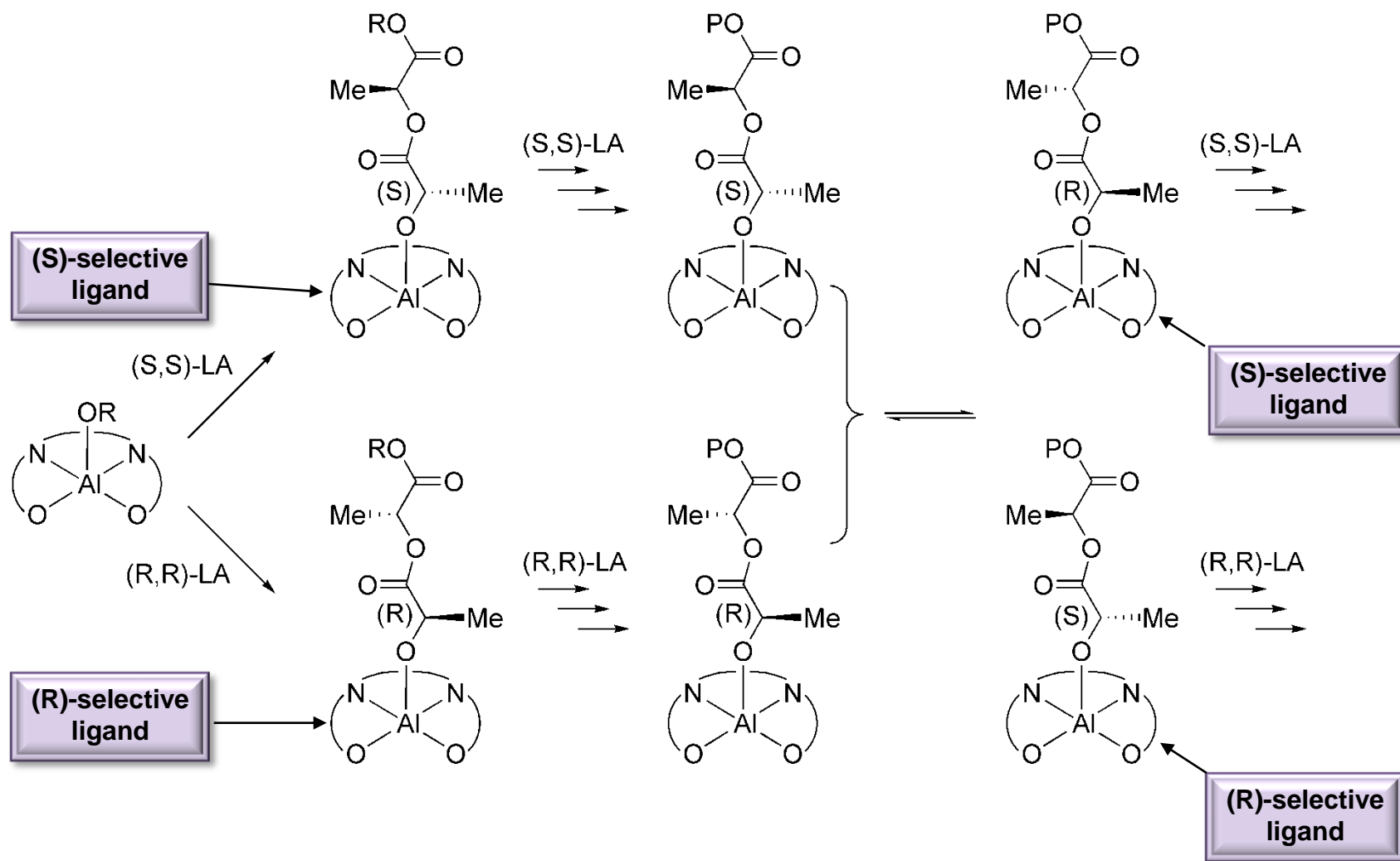
The stereocomplex myth



Smith and Baker: each enantiomer of the Al initiator preferentially consumes one monomer enantiomer and the isotactic chains of all ...RRRRRR... and all ...SSSSSS..., which then crystallise into a stereocomplex.

Coates: each enantiomer of the initiator preferentially consumes one monomer enantiomer, giving short sequences of ...RRRRRR... and ...SSSSSS... but these can exchange between metal centres.

Formation of isotactic PLA from chiral salen Al initiators



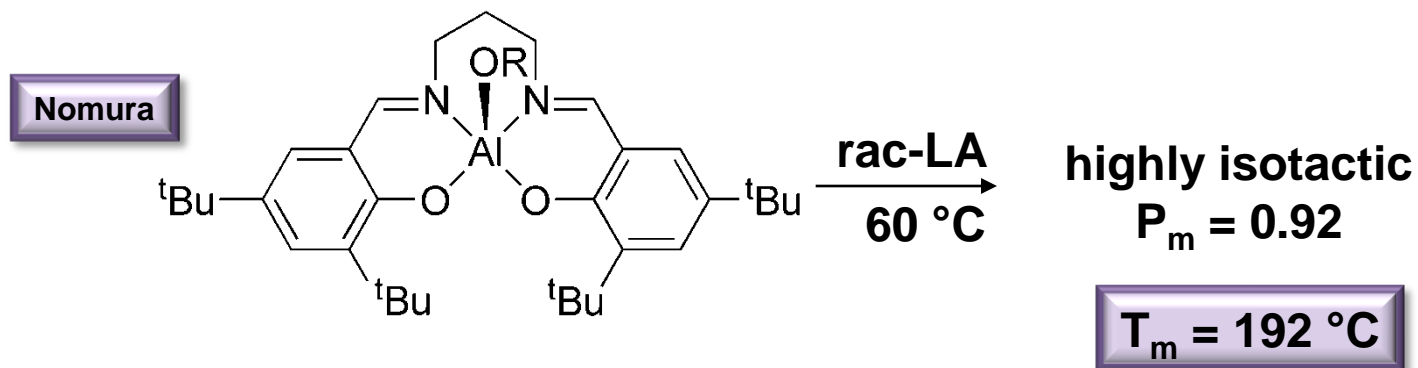
The PLA product is not a stereocomplex -
it is a stereoblocky copolymer:
-(RR...RR)-(SS...SS)-(RR...RR)-(SS...SS)-

Elevated T_m values arise from
cocrystallisation of short isotactic domains

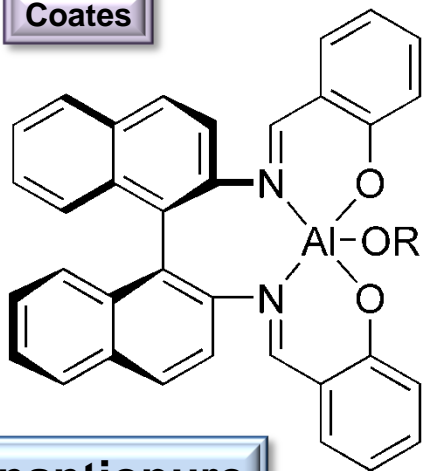
In theory, if you could stop the exchange of polymer chains
between the metal centres, then all R and all S chains would be
obtained and these could then form the stereocomplex material

Let's return to achiral salen Al initiators

Numerous achiral salen ligands have been investigated (24 examples are reported in our recent paper:

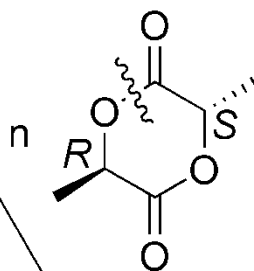


Coates

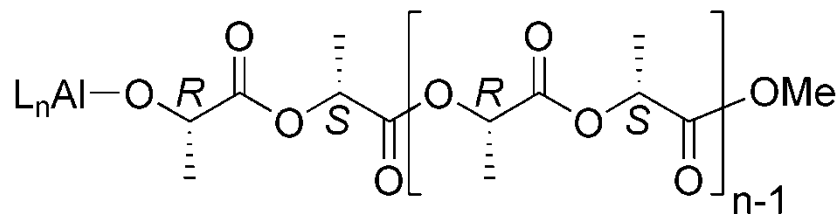


enantiopure

Preferentially consumes (*R,R*)-LA instead of (*S,S*)-LA (see slide 12)



\therefore *meso*-LA selectively cleaved at acyl bond adjacent to (*R*)-methyl



1. Salen-supported Al-based initiators nearly always give highly isotactic PLA (from the racemic monomer).

ligand-assisted chain end stereocontrol

2. The isotactic product is actually a stereoblocky material, not a stereocomplex. T_m values are therefore higher than for isotactic poly(L-lactide), but lower than for the stereocomplex.

3. Syndiotactic PLA may be prepared from meso-lactide using a chiral salen ligand (with a 2,2'-diaminobinaphthyl backbone).