


## ESR 5

<b>Project title and research strand:</b>	Self-assembling in Poly(hydroxyalkanoate)s Strand 3: functional polymers	
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### Abstract

The adoption of bio-based polyesters like poly(L-lactide) (PLLA) and polyhydroxyalkanoates (PHAs) is hindered by low crystallization rates, causing thermal instability and brittleness. Hydrogen-bonding oxalamide-based compounds (OXAs) have been synthesized as nucleating agents to enhance crystallization in these polymers. OXAs dissolve into the polymer matrix, self-assembling during cooling to provide surfaces for heterogeneous nucleation. The nucleation mechanisms were investigated under quiescent and flow conditions using thermal, morphological, rheological, and conformational techniques, enabling the construction of phase diagrams for two OXAs. Flash Differential Scanning Calorimetry (FSC) and small-angle X-ray scattering (SAXS) under shear conditions were pivotal in interpreting nucleation behaviors. OXAs' nucleating ability depends on parameters like concentration, undercooling, interface, and molecular weight, suggesting surface-driven and stretch-induced rather than epitaxial nucleation. In PLA stereocrystals, epitaxial growth was observed, with mechanisms studied using wide-angle X-ray scattering (WAXS), Transmission Electron Microscopy, and Nano XRD at the European Synchrotron Radiation Facility (ESRF). Additionally, the thermostability of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) has been studied and improved to mitigate degradation from biosynthesis residuals and expand their processing windows. Finally, a polyolefin system is studied with the ultimate nucleating agent (KB25) as a proof of concept, demonstrating that growth in one dimension is the most efficient.



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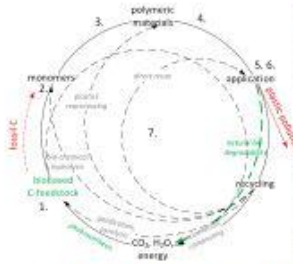


# Molecular design of nucleating agents and their self-assembly in biobased polyesters

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## The role of bio-based polyesters



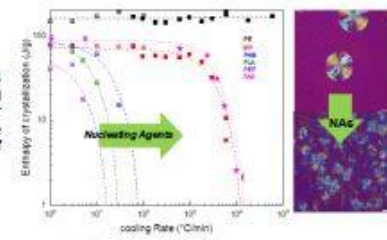
The great potential of biobased polyesters, such as polyhydroxyalkanoates (PHAs), polylactide (PLA), and polyethylene furanoate (PEF), lies their characteristic of biodegradability, the intrinsic chemical recyclability and promising properties for various applications. However, their crystallization rates do not align with industrial cooling rates, resulting in large crystallite sizes and incomplete crystallization.

- This leads to:
- Thermodynamic instability
  - Poor mechanical properties (e.g. brittleness)
  - Haziness

To tackle these issues, a novel class of nucleating agents (NAs) has been developed<sup>1,2</sup>, specifically hydrogen-bonding oxalamide-based compounds (OXAs). The nucleation efficiency depends on their molecular design, which influences factors such as melt miscibility, phase separation temperatures, and the structure and morphology of the self assembled NA.<sup>3,4</sup>

With the aim of achieving optimum molecular and structural design and to align it to the thermo-mechanical properties of different biobased polyesters, transitioning systematically from PLA to PHAs, the question that needs to be answered is:

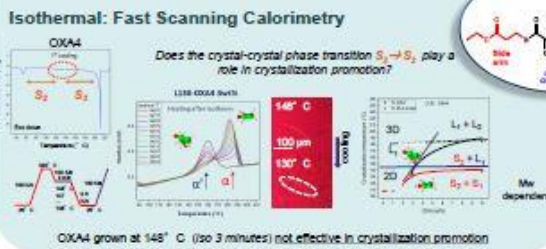
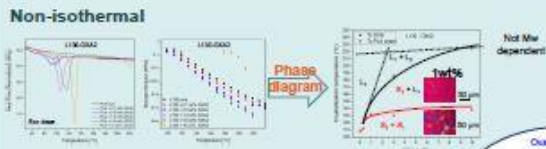
**What is the fundamental mechanism of nucleation?**



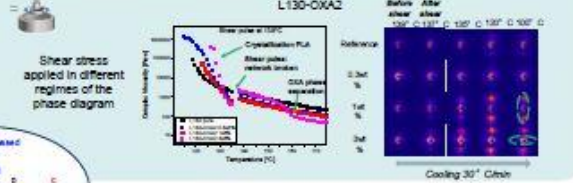
## Potential mechanisms

- Stretch induced (entropy)
- Hard epitaxy (specific crystallographic orientation)
- Soft-epitaxy (surface energy/roughness)<sup>5</sup>

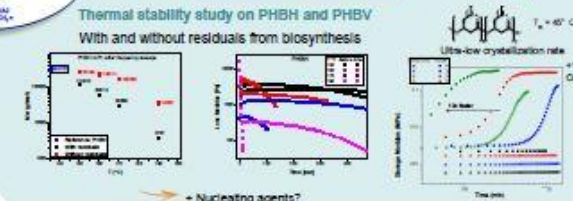
## From PLA in quiescent conditions..



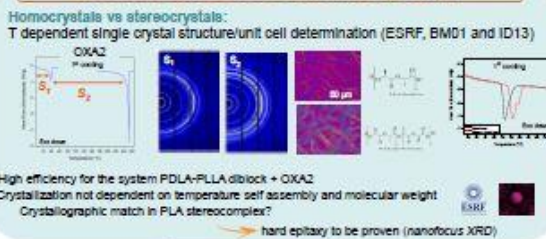
## ..and under defined flow conditions



## ...to PHAs



## ..to diblock PLLA-PDLA: hard epitaxy?



## ...to the ultimate 1D NA assembly: PP-PE case study



## Conclusions and outlook

- The promotion of crystallization in the studied systems is likely entropy-driven, not induced by epitaxy; synergic effect of polymer relaxation time and NA growth rate;
- The phase transition observed in OXA-4 plays a role in the nucleation mechanism, because of the different conformation of the molecule;
- Depending on the regime in which the shear pulse is applied, either the OXA assembly or the PLA crystallization is promoted
- Surface energy via 1D NA assembly favored
- Possible wide application of concept/chemistry thanks to the knowledge gained by the investigation of these systems

References

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