Title: Finding the key to enzymatic degradation of macromolecular crystals in solving plastic pollution

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Introduction: Plastics are energy efficient materials that provide sustainable solutions on the one hand, but are a threat to biodiversity and life on the other. While closing plastic carbon cycles timely relies on selection of biobased building blocks, plastic pollution jeopardizes the closure of cycles and moreover life. Biodegradable polymers exist, typically polyesters that can be derived from natural and fossil resources. However, these polymers either (i) need human intervention by raising temperature above the glass transition temperature (Tg) (e.g. polylactides) in industrial composting, or (ii) are uncontrolled biodegradable since the Tg is "permanently" below ambient temperatures. Timing and/or triggering biological degradation only when plastics end up in nature remains elusive. Inspired by silk the approach is based on controlled, water actuated enzymatic degradation, excluding human intervention. Crucial is the degradation of polymer crystals to prevent formation of micro-plastics, though the mechanism is barely understood to date. Why are some polymer crystals naturally degradable and others not? What is the role of crystal structure on the enzymatic degradation of polymer crystals and how should the design rules in materials engineering change?

Hypothesis and Objectives: Molecular mobility in the non-crystalline domains above Tg is trivial for the polymer chain to adapt molecular conformation and configure to the active site of enzymes. Inspired by silk, we propose polyamides where a water dependence of Tg, can (i) be tuned via polyamide polarity and (ii) used as actuator of biological degradation in nature. The role of crystal surface chain topology on operating modes of enzymes and consequent degradation rates were reported for polyhydroxyalkanoates crystals by Hocking et al (Macromolecules, 1996). It is also known that low crystallinity and small crystallites are in favour of biodegradability, but are technically on the expense of mechanical performance – however not in silks. Little is known on the role of relative crystal dimensions and interaction between neighbouring molecules within a crystal, enthalpy, while a closer look to scattered literature data and our recent lab work, based on defined crystal dimensions and surface chain topology in silk fibres, polyglycine crystals (a model for silk crystals), polyamide 6 crystals and fibres, hint to enthalpy in combination with crystal dimensions. Following this approach we wish to understand the cause for biodegradability of polymer crystals and how to design processing conditions to realize these biodegradable polyamide crystals without sacrificing performance.

Setting and Methods: Work will be performed in the Institute located at the center court of Brightlands Chemelot Campus, in the surroundings of industrial corporate R&D and in collaboration with Aachen University (RWTH, Germany). After characterization of the crystals by (ultrafast) differential scanning calorimetry (DSC), X-ray diffraction (XRD), AFM and FTIR and solid state NMR spectroscopy, progress in enzymatic breakdown will be visualized by polarized optical microscopy (POM), atomic force microscopy (AFM), profilometry, electron microscopy (TEM, ESEM). Gel Permeation Chromatography provides insight in molecular weight changes.

Impact: Plastic pollution results from inappropriate recycling, threatening life and postponing closing afore-mentioned cycles. Complementing energy efficient processing of polymers by selecting biobased feedstock the newly developed structural design of plastic, naturally degradable products close the cycles technically.

Requirements candidate: The candidate having passion to research should have background in physical chemistry and in particular in polymer physics.

Selected five publications of the supervisor: https://scholar.google.co.uk/citations?user=b79ixaoAAAAJ

1. **Nature Materials** 2005, *4*, pp 635−641. DOI:10.1038/nmat1437 (citation 192)
2. **Nature** 1991, 353 (6339), 55-57 (citation 66); **Nature (news & views)** 2000, 404 , 134-135 (citation 93)
3. **Physics Review Letters** 2008, 100 (4), 048302-48305 (citation 122)
4. **Carbon** 2006, 44 (4), 778-785 (citation 306)
5. **Macromolecules** 2012, 45, 5789-5797 (citation 12)