

## **Projects within the DPI Polyolefins programme**

### **Project #801: Predictive modelling of mechanical anisotropy in oriented semi-crystalline polymers directly from morphological characteristics (OrientXpress)**

*In this project, a quantitative structure–property relationship will be developed for flow-oriented semicrystalline polymers, in particular polypropylene (PP), in terms of the fully anisotropic yield kinetics and the underlying oriented macromolecular structure. This will involve (i) the incorporation of an oriented amorphous phase in a micromechanical model and (ii) the characterization of the slip kinetics for the individual slip systems of a semicrystalline polymer and their effect on macroscopically anisotropic yield kinetics. This way, a scale transition between the physical mechanisms of deformation and the micromechanical performance of oriented semicrystalline polymers is obtained.*

---

### **Project #803: HEat Management in Polymerization Reactors (HEMPR)**

*Gas phase polymerization processes are limited by the rate of heat removal, which is typically done by injecting and evaporating liquid droplets. This project experimentally and numerically investigates the implications of the droplets on the behavior of the gas and solids phases, e.g. on the hydrodynamics, formation of agglomerates, heat transfer, and on the process operation as a whole. Multi-scale models, from fully-resolved particle-droplet interactions to meso-scale discrete particle simulations, will be developed and used to simulate and optimize the heat management in these reactors under industrially relevant conditions. Various optical/infra-red experimental techniques are used for model validation and verification.*

---

### **Project #804: From homogeneous to “colloidal” olefin polymerization catalysts: effects of mass transport limitations on reaction kinetics and polymer microstructure (CollCats)**

*This project aims to explore, in the framework of a collaboration between chemists and chemical engineers and with a combination of experimental and theoretical tools and methods, the hypothesis that the entrapment of molecular olefin polymerization catalysts inside the produced polymer can limit monomer transport to the active centers as soon as the system becomes “colloidal”, i.e. earlier than polymer precipitation is clearly perceived. If this is proved true, conventional kinetics should be revised, and a number of puzzling observations could find simple explanations (just to mention a few: (a) the (much) higher chain propagation rates measured in Quenched Flow experiments compared with conventional ones; (b) the so-called “comonomer effect” in “solution”; or even (c) the broad or multimodal molar mass and/or comonomer sequence distributions obtained with certain single-center catalysts).*

---

### **Project #810 Online Polyolefin structuring during Cast Film Extrusion (OP\_CaFE)**

*The effect of processing conditions, polymer chain structure and additives on the final structure of polyolefin films will be studied to establish the structure/property relationships for cast film extrusion. Ex-situ microbeam and depth-resolved scattering techniques will be employed to analyze the film structure with high spatial resolution. Furthermore, a method to study in-situ the polymer structuring during cast film extrusion using synchrotron X-rays will be developed. Furthermore, the effect of different nucleating agents will be studied since it seems that a combination of optimal processing parameters and heterogeneous nucleation can lead to improved and stable optical properties.*

---

**Project #813 Multi-scale investigation of silica-supported ethylene polymerization catalysts during the early stages of the reaction (MULTIPOL)**

*We aim to research Ziegler-Natta and metallocene-based polymerization catalysts in the early stages of the genesis of active sites and polymer formation by a multi-scale characterization approach under reaction conditions. Two PhD students will jointly work together on the same set of solid catalysts; one, based at Torino University, focusing on catalyst ensemble characterization, while the second, working at Utrecht University, will perform single catalyst particle characterization. Thereby we aim to link the macroscopic physical (e.g. mechanical strength and temperature gradients) and chemical (e.g. polymer composition, type and density) properties with nanoscopic chemical properties (e.g. oxidation state and coordination environment).*

---

**Project #814 Control of crystallisation, chain entanglement and rheology via process conditions (DisEntangled)**

*Evidence shows that polyethylene (PE) chain (micro)structure (entanglement, MWD, nascent crystallinity) is influenced by the choice of the continuous phase; the degree of swelling appears to have a significant impact on these competing phenomena. We will focus on the use of supported catalysts, and study in situ swelling by different condensed and vaporised diluents on PE. DMA, thermal, mechanical, and spectroscopic testing will be used to characterise entanglements for high MW polymers, and proton NMR will be used for soluble PE1. The feasibility of a gas phase UHMWPE process will be explored.*

---

**Project #815 Augment the macroscopic PROperties of i-PP composites by controlling the microscopic Fiber-matrix Interactions via Transcrystallization (PROFIT)**

*Fiber-reinforced semi-crystalline polymer composites are largely employed for their improved strength with respect to the unfilled polymer matrix. The adhesion and mechanical interaction between the polymer and the fiber are known to play a key role in determining the mechanical behavior of the final product. Heterogeneous nucleation on the surface of the solid fiber, together with stresses induced by matrix shrinkage upon cooling, is thought to positively affect the matrix/fiber interaction. In this project we aim to systematically relate the formation of transcrystalline layers at the fiber/matrix interface to its bulk mechanical properties via microscopic observations, both during processing and micromechanical testing.*

---

**Project #816 Correlation between process-induced crystallization and mechanical properties in injection molded isotactic polypropylene (iPP) (ProCrystal)**

*In injection-molded parts, the development of skin-core morphologies due to large gradients of cooling rates is well known. Additionally, specific layers occur due to the flow conditions. The interrelation between the locally different structure and global mechanical properties is one keypoint to obtain new application fields and therefore of high scientific and technological interest. This project focuses on the application of new experimental tools like fast scanning chip calorimetry to character-*

ize crystallization/solidification at processing-relevant conditions in thin-walled molded parts, analysis of flow-induced crystallization and local structures of moldings by microscopy and X-ray scattering. These data will be used to optimize the injection-molding process such that solidification in the various zones of the molding occurs at pre-defined temperatures and strains, in order to tailor formation of specific local structures and with that of properties like the flexibility of film hinges. The link between the experimentally determined crystallization kinetics and the injection-molding process is intended to be predicted by the application of simulation tools. Controlling the semi-crystalline morphology of injection moldings from new isotactic polypropylene (iPP)-based materials gives the opportunity to improve disadvantageous properties of the weakest region of moldings like flow hinges, serving as a sensitive measure of the success of the approach.

---

### **Project #817 An inter-disciplinary high-throughput approach to olefin block copolymers (HT-OBC)**

Progress in polyolefins has always been the outcome of multi-disciplinary efforts; most success stories are characterized by fine control on all individual elements in the chain-of-knowledge, from catalysis to end-use properties. With growing complexity, though, the field calls for (more) holistic approaches with a higher throughput. Olefin Block Copolymers (OBCs) produced by ‘chain shuttling’ are an exemplary case; understanding these materials, which are innovating the LLDPE market, is virtually impossible without considering polymer chemistry and physics together. In this project, the intricate and still poorly defined OBC structure-properties relationships will be unraveled by means of an inter-disciplinary high-throughput approach with disambiguation loops encompassing adjacent elements of the chain-of-knowledge; this also includes an important tool implementation part. The proposed method can become a paradigm in future investigations of novel materials from complex catalytic routes.

---

### **Project #830: Electrostatic charging of polyolefin powders on the level of particles (EstatCharge)**

Triboelectric charging is a key phenomenon affecting particle agglomeration and wall sheeting. The project aims to quantitatively describe the charging of polyolefin particles caused by both particle-particle and particle-wall collisions. Experiments will focus on: E1) effects of material properties on charging – particle size distribution, surface roughness, temperature-dependent properties, excitation of surface electron states; E2) effects of interface on charging – humidity, antistatic agents, gas/liquid composition; E3) charge neutralization. The obtained knowledge will be simultaneously utilized in the development and validation of three levels of charging models and agglomeration models.

---

### **Project #831: Molecular modelling of stretch-induced crystallization in polyethylene and polypropylene layers (PO-Stretched)**

Flexible plastic packaging is the fastest growing segment of the packaging industry. Designing easily recyclable and energy efficient products is the challenge of the modern circular economy. Polyethylene (PE) and isotactic polypropylene (PP) are important plastics, but achieving a suitable combination of impact resistance, stiffness and toughness in all-PE multilayer packaging and filled PP has been a persistent challenge. In the PO-stretched project we will undertake multiscale simulations of semicrystalline morphology development upon high-strain mechanical deformation of polyethylene and polypropylene, to understand the mechanisms controlling crystallization, toughness, permeability, determine optimization design strategies and provide a molecular basis for finite-element simulations.

### **Project #832: Quality model for COntaminated Recycled Polyolefins (Q-CORP)**

*Q-CORP entails the development of a multi-factor quality model for the mechanical recycling of contaminated polyolefins. As contaminations we consider either (up to 20%) other polymers, introduced by multilayer packaging or imperfect sorting, or smaller amounts of components like inks, labels or barrier layers. The model is based in polymer science and will take aspects from miscibility, polyolefin chain architecture and deformation mechanisms to come to a predictive output that gives insight into potential applications for the recycled plastics. As such, it can be used for Design for Recycling (by product designers) as well as fit for-use sorting (by sorters/recyclers).*

---

### **Project #834: RHEOlogical determination of POLyolefin Architectures (RHEOPOLAR)**

*Determining the molecular structure of polyolefin-based materials is a relevant scientific and technological challenge. Molecular weight, its distribution, and structural details are fundamental parameters for materials design and processing, but often difficult to ascertain. The main objective of RHEOPOLAR is to study the molecular details of specific polyolefin-based systems through an innovative rheological approach. Linear and non-linear rheology will be measured in concentrated, entangled solutions, instead of melts, thus overcoming some intrinsic experimental difficulties encountered in measuring the latter. Molecular models and constitutive equations for entangled solutions will be used to extract the quantitatively relevant microstructural information.*

---

### **Project #835 Quantitative Structure-Activity Relationships (QSAR) in Post-Metallocene-Based Olefin Polymerizations Using Chemically Meaningful Computational Descriptors (POST\_MET\_QSCAR)**

*This project aims to develop predictive 'clear-box' QSAR models of selected post-metallocene olefin polymerization catalysts with octahedral transition metal centers. In a previous DPI project (#800) a research strategy integrating parallel precatalyst synthesis (MSU), high-throughput catalyst screening and QSAR modeling (UniNa) and focused mechanistic investigations of active species in solution by means of advanced NMR techniques (UniPg) was successfully applied to stereorigid C<sub>2</sub>-symmetric ansa-zirconocenes of 'Spaleck-type'. As a result, novel catalysts with improved performance were identified, notwithstanding the reputation of said catalyst class to have been fully optimized. The challenge here will be to demonstrate that the same approach can work also in the much more demanding case of catalytic species typically characterized by equilibria between several different isomers, some of which are dormant/inactive.*

---

### **Project #836: Practical, High Throughput Quench Labeling Techniques for Information-Rich Analysis of Alkene Polymerization Catalysts (CAT\_ChromQL)**

*Accurate active site counts<sup>1</sup> and kinetic models<sup>2</sup> of catalytic alkene polymerization are essential to understanding modern processes. Sensitive, quantitative detection of distributions of live polymer chains, dormant chains, and dead chains with reaction time enables practical determination of these critical attributes. Chromophore quench-labeling (CQL) selectively and covalently tags live polymeryls with a strong UV absorber. Dual detection GPC reveals two*

*MMDs: RI detection senses all polymeryls and UV detection selectively measures live polymeryls. This proposal extends the CQL technology to mixed NMR and UV analysis, high temperature GPC for analysis of polyethylene and polypropylene samples, and high throughput experimentation.*

---

**Project #846: In-Chain Functionalized Polyethylenes from Controlled Free-Radical Polymerization under Benign Conditions (INRAD)**

*Endowing polyolefins with low densities of in-chain functional groups can enhance their compatibility in the broadest sense, enable chemical recycling approaches and overcome environmental persistency. However, an introduction of such groups during ethylene polymerization in an efficient way is challenging. This research addresses the incorporation of keto groups from carbon monoxide comonomers, in particular complemented by in-chain ester groups. Limitations identified in our preliminary work are addressed by an insertion mechanism of the so far rate limiting step in a controlled radical chain growth scheme through novel initiator/catalyst systems. Microstructures and fundamental materials properties of the target polymers are elucidated.*

---

**Project #847: A microstructural insight in polyethylene based bioriented mono-materials: from fundamental to processing (PER-MANENT)**

*The aim of the project is the identification of the rules for controlling the crystalline-microstructure, that is the crystalline thickness, crystalline orientation and the chain topology in the amorphous regions, which develops in biaxially stretched polyethylene samples (PE) having different chain-microstructures as a function of processing conditions. The research will focus on BOPE films processed using both industrially- and lab-relevant conditions. Advanced experimental and analytical methods for structural and mechanical analysis paired by modelling will be employed. The identification of these rules will allow planning new processing protocols to extend PE usage as mono-material in unprecedented and challenging applications.*

---

**Project #848: Ziegler-Natta Catalysts for Polypropylene with Temperature-Controlled ID/ED Compositions (ZN/TCLB)**

*Ziegler-Natta catalysts for the production of isotactic polypropylene are formulations in which  $TiCl_4$  and an organic Lewis base ('Internal Donor', ID) are co-adsorbed on a nanostructured  $MgCl_2$  support; this solid precatalytic phase is subsequently contacted with an  $AlR_3$  activator, usually complexed with another organic Lewis base ('External Donor', ED). The stereoselectivity follows from the inherent chirality of alkylated surface Ti species, sterically enforced by adjacent ID and/or ED molecules at nonbonded contact. Some IDs (e.g. aromatic or aliphatic esters) react with the  $AlR_3$  under polymerization conditions, and desorb from  $MgCl_2$  surface; when this is the case, the action of active site modification is dominated by the ED. To the best of our knowledge, no attempts to purposely modulate ID/ $AlR_3$  reaction kinetics have been reported so far. In this project we aim to design IDs with a desired temperature dependence of the reaction rate with  $AlR_3$  compounds: 'slow' up to e.g. 80°C, 'fast' above e.g. 100°C. When this condition holds, we expect that the composition of the ID/ED pool in polymerization can be finely and continuously tuned between the two extremes of neat ID and neat ED by means of a high-temperature pre-activation treatment with  $AlR_3$ /ED mixtures. Furthermore, we plan to design the chemical structure of the IDs so as to regulate their chemisorption affinities for different  $MgCl_2$  lattice terminations, thus inducing desired surface topologies. The resulting catalysts*

*should feature distributions of catalytic species and polymer product properties that can be easily modulated in unusually wide ranges.*