

## LINKING PROCESS CONDITIONS WITH POLYMER PROPERTIES FOR LDPE PROCESSES

Kristina Maria Pflug, Technische Universität Darmstadt  
Kristina.Pflug@pre.tu-darmstadt.de  
Markus Busch, Technische Universität Darmstadt

**Key Words:** modelling, structure-property relationships, LDPE polymerization, kinetics, rheology  
Low Density Polyethylene (LDPE) is a polymeric material of great importance on the global market. Its applications range from commodity purposes such as films, tubes and packaging to the specialty sector including medical products such as implants. One of the characteristics of LDPE is its unique polymeric microstructure exhibiting short- as well as long-chain branching (SCB and LCB) and a broad molecular weight distribution due to the free radical polymerization conditions. The polymeric microstructure of the polymer is mainly dependent on the polymerization process conditions and determines the final product properties and thus also the application area. However, experimental investigations of the free radical polymerization of ethylene are very costly due to the high-pressure (up to 3000 bar) and high-temperature (up to 300°C) conditions. Thus, there is a need for a simulation-based tool to link the process conditions with the resulting LDPE properties.

This work presents the successful implementation of a three-step multi-scale modelling approach to reach this aim. A visualization of this approach as well as the benefits of the individual steps is depicted in figure 1. The first step consists of modeling the complex kinetic network of the free radical polymerization of ethylene. Kinetic coefficients can be taken from literature [1] and the numerical solving of the resulting system of differential equations is conducted by the software *Predici* [2]. This yields average product properties, such as branching densities per 1000 carbon atoms (SCB/1000C and LCB/1000) as well as the molecular weight distribution. Those can be validated against <sup>13</sup>C-NMR measurements as well as high-temperature size-exclusion chromatography.

The Monte Carlo simulations conducted within this work are a hybrid stochastic approach. This means that so-called reaction frequencies can be exported from the deterministic simulation and then serve as input for the stochastic modelling of the polymeric microstructure. Although an individual macromolecule approach is applied – meaning that the macromolecules are simulated one by one – ensembles of several millions molecules can be generated within a couple of hours and lead to statistically significant results. In this way chain-length dependent properties – such as chain-length dependent branching densities, as well as the exact topologies of macromolecules are determined. Additionally, the application of a random walker on the topologies gives the three-dimensional extent of the macromolecules, which can be compared to and validated against light-scattering data (radius of gyration and contraction factor).

If the ensemble generated by the Monte Carlo simulation is reduced smartly, it can be used in the next step as input for modelling the melt rheology of the resulting polymer. Here, the branch-on-branch algorithm is used. [3] The linear regime of polymer deformation can be modelled and viscosity as well as storage and loss moduli can be validated against experimental data. Additionally, the non-linear shear and extension behavior of the polymer

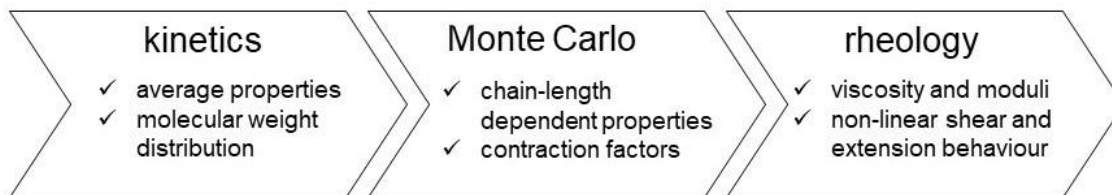


Figure 5 – Visualization of the three-step modelling approach used to link process conditions with LDPE properties.

can be investigated, which is especially relevant when it comes to predicting polymer processing. This approach has been implemented and validated for a mini-plant scale autoclave reactor operated under well-defined process conditions close to industrial relevance. Moreover, it will be shown that it is also directly applicable to any other reactor type, scale and initiation mechanism. This will be demonstrated by applying the three-step modelling approach to an oxygen-initiated industrial tubular reactor including the complete heat balance.

[1] T. Herrmann, *PhD thesis*, Technische Universität Darmstadt 2011.

[2] M. Wulkow, *Macromolecular Reaction Engineering* 2008, 2(6), 461-494.

[3] D. Read, D. Auhl, C. Das, J. den Doelder, M. Kapnistos, I. Victorias, I. and T.C. McLeish, *Science* 2011, 333(6051), 1871-1874.