

RATIONAL DESIGN OF POLYMERIZATION SYSTEMS: PERSPECTIVES FROM COMPUTATIONAL CHEMISTRY AND REACTION ENGINEERING

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The stochastic nature of polymerization processes often leads to a mixture of chain populations with drastically different molecular architecture. Things can be further complicated by reactor type and geometry, species involved, operating conditions, etc. Thus, scientists and engineers frequently rely on models to aid new and existing product development, scale-up, implementation and troubleshooting. Ultimately, detailed and accurate models enable the formulation of optimal reaction conditions to achieve desired polymer architecture and properties. This presentation will focus on examples from free radical and metallocene-type polymerization systems and provide insights into the rational design of materials.

The realization that any polymerization model is only as reliable as the kinetic, mass and energy balance parameters that it employs leads to the continuous improvement of the analytical techniques and instrumentation necessary to determine them. Even the simplest ideal kinetic models require accurate rate parameters to guide system development. Alas, obtaining those from experiments is not always practical and, in some cases, impossible. Computational chemistry provides an appealing alternative. Moreover, with the advances in high-performance computing, the investigation of larger species has become more tractable. These advances are of particular importance to industry where quick results are often needed to enable decision making. In the first part of this presentation, we will demonstrate a computational protocol for accurate rate parameter estimation in both gas and condensed phase. Special emphasis will be placed on the concept of multiple reaction pathways associated with the chemical transformations along the reaction coordinate (Figure 1).

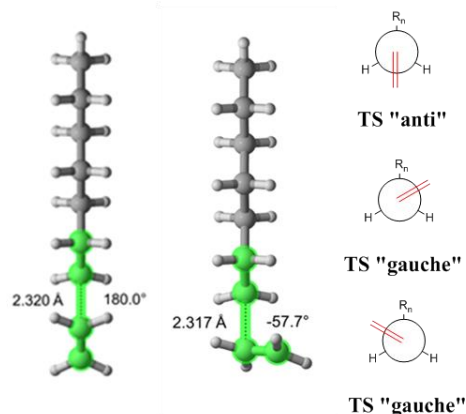


Figure 1– Multiple transition states for polyethylene propagation

While obtaining accurate rate parameters is essential to elucidate the polymerization mechanism, often, a

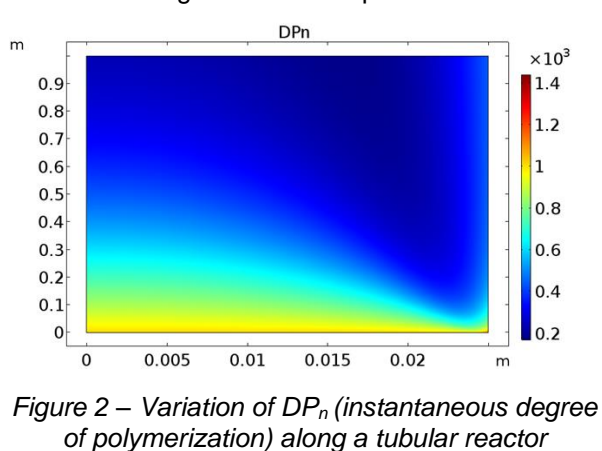


Figure 2 – Variation of DP_n (instantaneous degree of polymerization) along a tubular reactor

significant level of model detail and complexity is required to describe the overall material morphology. For example, in the synthesis of Linear Low Density Polyethylene (LLDPE), comonomers are responsible for reducing the density and crystallinity of the final material by introducing short side chains into the polymer backbone. However, higher comonomer levels typically decrease the molecular weight due to their lower reactivity as compared to ethylene. Hence, the strong dependency of key product properties on the composition can lead to undesired effects. To this end, we will show a reaction engineering approach to study the changes in the polymer composition and molecular weight distributions under various operating conditions (Figure 2).

Moreover, the choice of reactor geometry may also considerably impact the overall material properties. While tuning process variables such as temperature and relative

monomer concentration is important, catalyst selection (i.e. reactivity ratios) is paramount to achieving products with the desired composition and molecular weight distribution.