# A MULTI-SCALE TOOL FOR FUNCTIONALIZATION OF POLYOLEFINS THROUGH RADICAL GRAFTING

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## ABSTRACT (10 pt)

Free radical induced grafting of polymers is an important synthesis strategy to improve the properties of the pristine polymer and to ensure compatibility in blends. In this contribution, a multi-scale modeling tool is presented that enables to describe the grafting kinetics with a detailed description at the molecular, micro- and meso-scale combined with a 1D macro-scale reactor model. The potential of the model is illustrated with polyolefins as polymer substrate, including model validation to lab-scale and industrial scale data. It is highlighted that the model is indispensable to achieve the optimal process conditions for improved process intensification and functionality/molecular control.

**Key Words:** REACTIVE PROCESSING, TOPOLOGY, KINETICS, MULTIPHASE MODELING

## 1. INTRODUCTION

In today's society, polyolefins such as polyethylene and polypropylene are important polymers. An issue can be there compatibility with more polar compounds. To solve this issue one can consider a polymer medication after the first synthesis step. A key technique is free radical induced grafting (FRIG) in which as illustrated in Figure 1 initiator radicals are generated from a conventional radical initiator and subsequently these radicals abstract hydrogen atoms from the pristine polymer. The obtained mid-chain radicals (MCRs) can then under grafting by chain initiation and further propagation with vinyl monomer. Chain growth is ended upon termination reactions or another hydrogen abstraction. The overall product is a mixture of unmodified, grafted and crosslinked chains, with their balance related to the reaction conditions.

The identification of the relation of reaction conditions and the molecular structure and thus processability is far from trivial and the only pathway to maximize the degree of success is a synergetic combination of experimental and modeling work, acknowledging the additional complexity that arises due to diffusional limitations under melt processing conditions and mass transfer between multiple phases due to the overall time scale of the process. Limited focus has however been paid to the detailed characterization and design of multiphase FRIG of polyolefins. Either intrinsic kinetics are assumed or the reaction scheme is simplified or a single phase reaction mixture is considered in any case. Often the kinetic description is also restricted to only the monomer conversion or average characteristics such as the grafting density. This can be partially explained by the complexity of reactive processing but also by the limited computer capacity several decades ago [1]. Only more recently it has become clear that advanced kinetic Monte Carlo simulations allow to track individual molecules and thus the description can be lifted from an average to a detailed on at the molecular level. In the present work, it is illustrated how these recent developments have led to a state-of-the-art modeling

platform for FRIG of polyolefins. For simplicity focus is on a one-dimensional reactor description
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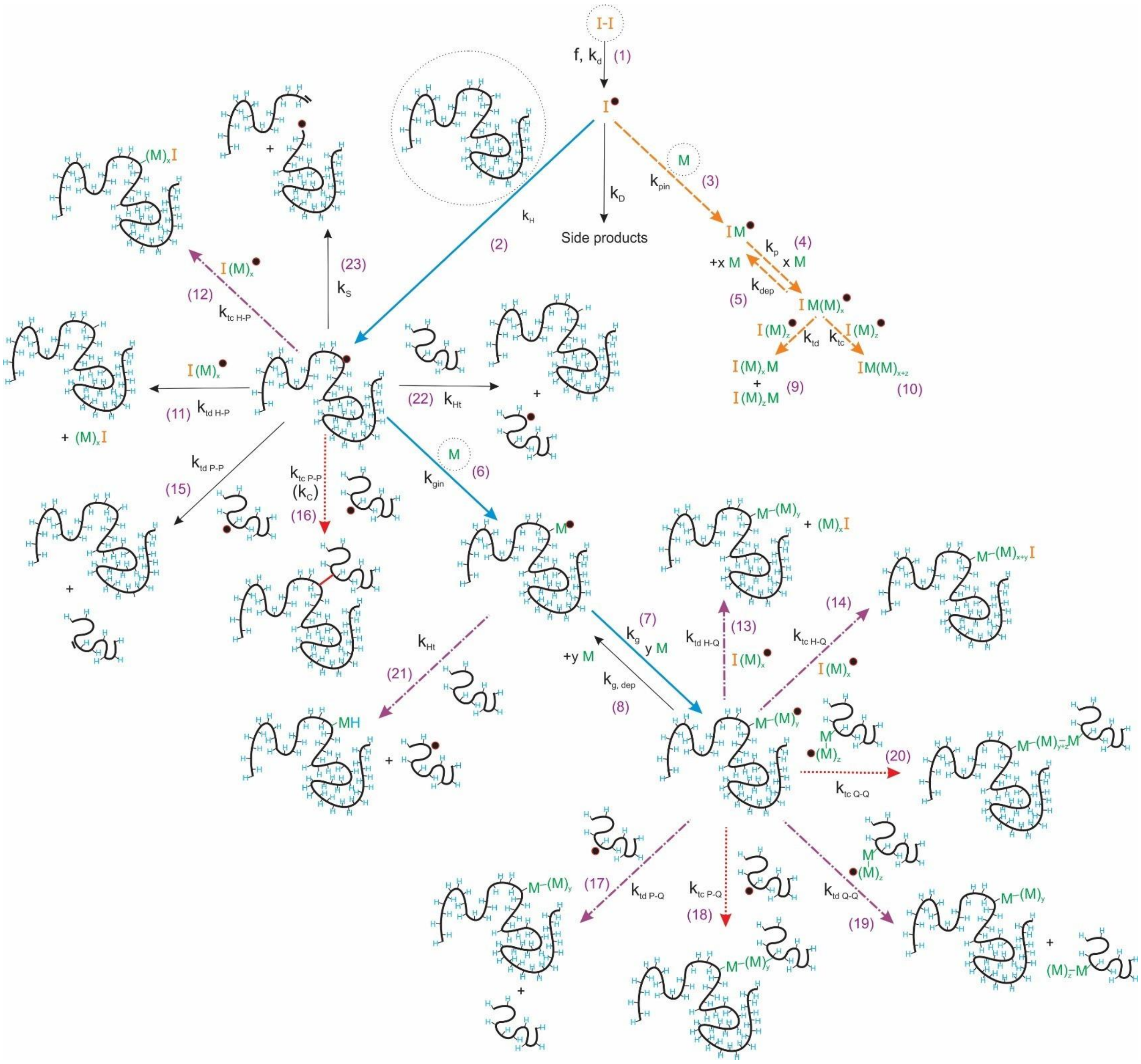

**Figure 1.** Reaction scheme for free radical induced grafting (FRIG) of polyolefins; shown for case of linear polyethylene.

## 2. RESULTS AND DISCUSSION

The FRIG kinetics under both single (long mixing times) and multiphase (industrial reactive processing time scales) reaction conditions are modeled according to the workflow in Figure 1 with 4 solvers (A-D). The core is the calculation of the reaction and possibly mass transfer events according to a kinetic Monte Carlo method with the full details provided in previous work [2]-[5]. The main concept is summarized here. According to the concept of binary trees the key FRIG properties can be obtained employing the main solver. This solver allows the prediction of parameters toward the evaluation of the extent of reaction, such as monomer conversion, functionalization selectivity and functionalization yield. Average properties for calculating the grafting and crosslinking are also obtainable, such as the average grafting density, the average chain length of grafts, and the average crosslinking density. In addition, the evolution of the chain length distribution (CLD) is possible. Solver B covers the reaction history of every individual macromolecule out of a representative initial number of polyolefin molecules, in parallel with Solver A. The enables access to the CLD of the grafted chains and the bivariate copolymer composition-CLD for the functionalized chains. Solver C accounts for the capabilities of Solver A or B complemented with mass transfer in case of phase segregation and a one-dimensional reactor description. Solver D enables the previous characteristics with additionally the possibility of several injection points and/or temperature zones.

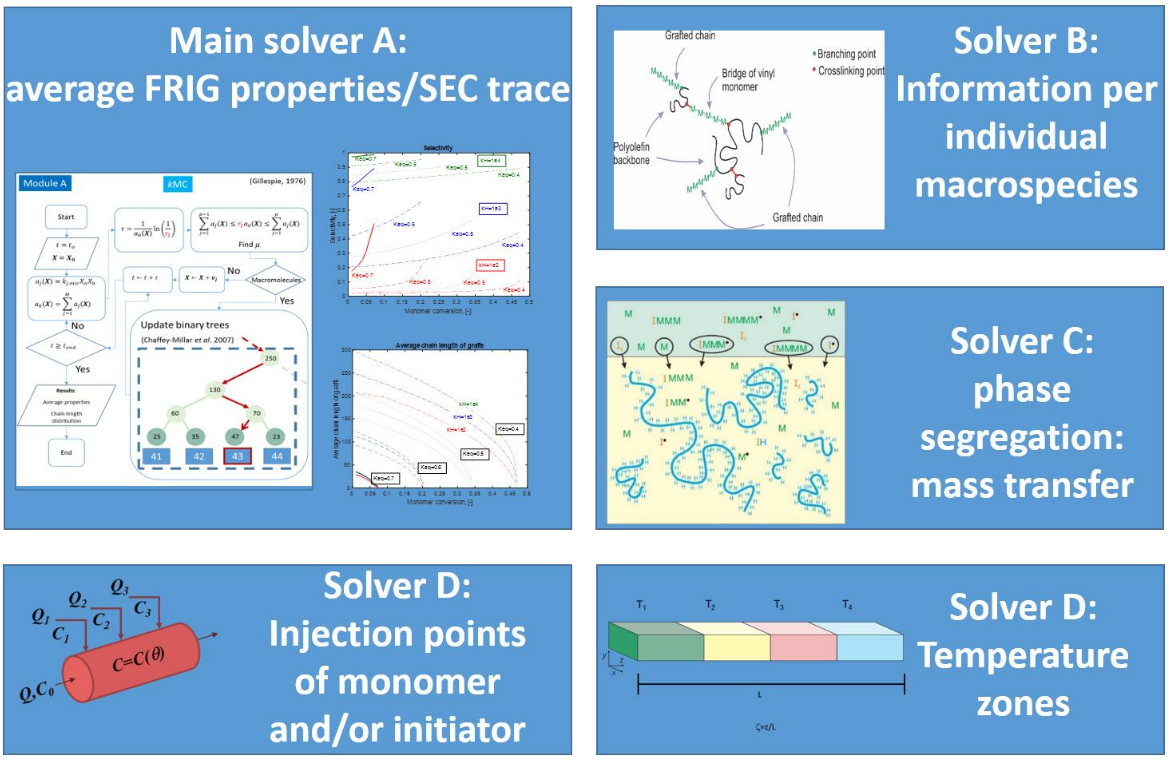

**Figure 1.** Workflow regarding modeling platform to describe FRIG kinetics under single and multiphase reaction conditions; the former can be mimicked by long mixing times; the latter result under time scale typical for reactive processing at industrial scale.

## 4. REFERENCES

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