PERFORMANCE ANALYSIS OF KINETIC MONTE CARLO ALGORITHMS FOR SYNTHESIS OF LINEAR POLYMERS

Alessandro D. Trigilio, Laboratory for Chemical Technology (LCT), Ghent University
alessandro.trigilio@ugent.be
Yoshi W. Marien, Laboratory for Chemical Technology (LCT), Ghent University
Mariya Edeleva, Centre for Polymer and Material Technologies (CPMT), Ghent University
Paul H. M. Van Steenberge, Laboratory for Chemical Technology (LCT), Ghent University
Dagmar R. D'hooge, Laboratory for Chemical Technology (LCT), Ghent University and Centre for Textile Science and Engineering (CTSE), Ghent University.

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The Gillespie-based[1] kinetic Monte Carlo (kMC) stochastic modeling has been proven to be a reliable tool to describe the time evolution of processes in many research fields. It aims at the exact solution for the rigorous chemical master equation and presents a simple but powerful tool that has been used in polymer reaction engineering to obtain a detailed macromolecular interpretation,[2-7] provided that advanced data structures are used to store the results and capture the required characteristics.

One of the main advantages of kMC is that all the molecules can be tracked completely, which can then be used to obtain detailed information about microscopic structures or chemical composition. The drawback of kMC is the relatively long simulation times for (1) complicated polymerizations (e.g., with branches or grafting) or (2) polymerizations with low-concentration species, which require considerably large control volumes. Concerning the process complexity, the main time bottleneck is sampling the distributed molecules that will react in a specific reaction channel. One of the main strategies to overcome this is to study and select the appropriate data structures to store the molecular information and carefully select a sampling method compatible with the chosen data structure. Regarding the control volume, to avoid dealing with over-detailed and thus long simulation times, it is critical to determine the minimal control volume that will lead to satisfactory results, free from the so-called stochastic noise, allowing a smooth representation of the response variables.

In this work, the leading test sampling methods for kMC are applied to typical polymerization processes to select the optimal method aiming to reduce the total simulation time. Specifically, the investigated methods are the linear search, d-tree search, q-section search (q and d ranging from 2 to 6), interpolation search (including higher order interpolations), and regula-falsi (see Figure 1).8-9 The polymerization processes used are free radical polymerization (FRP) of methyl methacrylate, nitroxide mediated polymerization (NMP) of styrene, and depolymerization via radical unzipping of poly(methyl methacrylate). Additionally, the different control volumes were used to propose a strategy to find the minimal control volume (thus the shortest simulation time) that allows a satisfactory representation of the response variables.

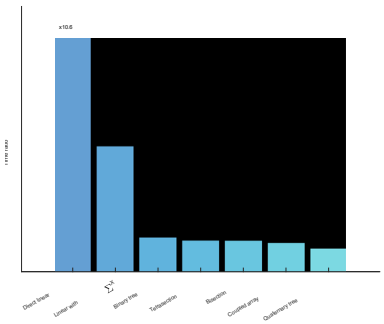

Figure 1. Simulation time ratio results for FRP for a selection of sampling methods, using the faster method as a reference.

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