A SIMPLE MONTE CARLO METHOD FOR MODELING ARBORESCENT POLYMER PRODUCTION IN CONTINUOUS STIRRED TANK REACTOR

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A dynamic mathematical model was developed to predict the molecular weight distribution (MWD) and branching distribution for arborescent polyisobutylene (arbPIB) in a continuous stirred tank reactor (CSTR). ArbPIB a promising biomaterial for human implantation [1] made by copolymerization of isobutylene and an inimer [2]. An inimer is a special molecule that contains an initiating group (initiator) and a vinyl group (monomer), which can form a T-shaped branch on a polymer chain. The model builds on a previous kinetic Monte Carlo (MC) algorithm developed for arbPIB production in a batch reactor [3]. A key innovation of our proposed MC approach is that inflow and outflow events are treated separately from reaction events, so that simulations are faster than would be obtained using existing approaches where inflow and outflow are treated as if they were reactions [4]. As such, we anticipate that the proposed methodology will be useful for other polymerization systems. To our knowledge, this is the first dynamic MC model for branched polymer production in a CSTR and the first model to predict the MWD of arbPIB in a CSTR, which tends to be much broader than the MWD of the corresponding batch copolymer. Model predictions are verified using a multi-dimensional method-of-moments model that predicts number and weight-average molecular weights, but not the MWD [5].

CSTR start-up was simulated beginning with fresh monomer and inimer in the reactor (no polymer at time zero). The model shows how the MWD continuously shifts to the high molecular weight region as time passes. For some operating conditions with relatively high inimer concentration or long residence times, the MWD does not reach steady state because larger and larger molecules that would eventually clog the reactor tend to form over time.

Figure 13 – Simulation results from CSTR with $[IM]_0 = 0.001 \text{M}$, starting from $10^5$ initial IM molecules, $[IB]_0 = 1.74 \text{M}$ and $1.74 \times 10^8$ initial IB molecules. A) MWD at i) 1200 s, ii) 2400 s and iii) 3600 s. The bold curve shows for the MWD generated at 7200s; B) Comparison of $M_n (\bullet)$ and $M_w (▲)$ calculated using the MC model with corresponding curves predicted using the multi-dimensional method of moments [5]