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Real-time Hybrid Monte Carlo Method for Modelling of 4 Monomer Semi-Batch Emulsion Copolymerization

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Abstract

Semi-batch polymerization processes are traditionally operated according to rigidly prescribed recipes prohibiting process optimisation and product property adjustment in real time. In this contribution, we focus on the development of computationally efficient model of 4-monomer semi-batch emulsion copolymerization for the use in model-based predictive control (MPC). We implemented a hybrid Monte Carlo approach consisting of two steps. First, the important process-product characteristics (conversion of monomers, reaction mixture temperature) are predicted by deterministic process model based on a set of ODEs; second, copolymer molecular architecture is generated using kinetic Monte Carlo simulation, utilizing state variables pre-calculated by deterministic model. The developed model was validated using various lab-scale recipes describing simultaneous copolymerisation of two hydrophilic and two hydrophobic monomers. Due to efficient implementation and program parallelization, the whole several-hours-long batch can be simulated within a few seconds resulting in a model applicable in MPC as a soft-sensor for the detailed molecular architecture of the produced copolymer.

Keywords: emulsion copolymerization, Monte Carlo modelling, on-line control, semi-batch reactor.

1. Introduction

Emulsion polymerization is usually carried out in a batch or semi-batch regime with fixed reaction recipe. In the past decades, there have been efforts to implement various advanced monitoring, optimization and control techniques in order to shift the production from recipe-based to state-based, i.e., to allow for the control of the production in real time. This can be done using nonlinear model predictive control (NMPC) systems, which rely on a robust, precise and computationally fast mathematical model of the system.

Various models suitable for online control of emulsion copolymerisation have been published (Valappil and Georgakis, 2002). They typically focus on the prediction of conversion, monomer concentrations, radical concentration in both phases and volume of both phases. These models are based on a set of ODEs and are fast enough to enable the on-line control of reaction temperature and optimization of batch time. However, concerning product molecular architecture, they provide only mean values of molecular weight distribution, because they are based on the method of moments. The detailed molecular architecture is essential for estimation of product properties, especially in the case of highly branched or cross-linked polymer. Moreover, the method of moments treats the polymer particle phase as a continuous domain, which may result in wrong molecular weight predictions. The emulsion copolymerization models were improved

(Plessis *et al.*, 2001) to deal with this so-called compartmentalization, but this method is computationally too costly for the use in models for MPC.

Although computationally more demanding, Monte Carlo (MC) methods are an alternative to ODE-based models, because MC models (such as presented by Arzamendi *et al.*, 2008) enable the detailed prediction of molecular weight distribution (MWD), branching density and other characteristics that determine material properties. These models usually compute every propagation step and/or every radical separately. Brandão *et al.* (2016) reviewed different MC approaches used in polymer reaction engineering. Some of them perform slightly better than others, but all require computational time comparable to the real semi-batch process duration (several hours). Such models are useful for off-line process optimisation, but not for on-line control. Tobita (1995) developed the so-called “competition technique”, which computes all radicals in one particle simultaneously and eliminates the propagation reaction step, and thus allows for significant reduction of MC simulation time, but his method has been applied only to homopolymerization systems with constant monomer concentration.

So far, no method has been both complex enough to accurately predict material properties and fast enough for on-line use. Here we combine Tobita’s competition technique and the ODE-based model into a hybrid Monte Carlo approach, which preserves accurate description of complex reactions in emulsion polymerisation, allows for varying temperature and dosing of monomer and initiator that is essential for MPC and provides results fast enough for MPC. Thus, our model is ready for use in an MPC of semi-batch emulsion copolymerisation reactors.

2. Model Description

Our system of interest is a seeded semi-batch copolymerization in monomer-starved regime. It is a complex system, involving two water-soluble and two water-insoluble monomers. The reaction mixture generally consists of three phases: aqueous phase, monomer droplets and polymer particles. Aqueous phase contains hydrophilic monomers and oligomers, initiator and radicals (decomposed initiator or a growing oligomer). Due to monomer-starved conditions, monomer droplets are typically present in a negligible amount; however, their balance is included in the model. Solid polymer particles are swollen by hydrophobic monomers. The essential part of the reaction recipe is also surfactant, which helps to stabilize the particles or monomer droplets but does not influence the polymerization process (i.e., secondary nucleation of polymer particles is neglected).

Our hybrid MC model consists of two parts. First, deterministic reactor-scale model based on a set of ODEs predicts evolution of temperature and concentrations in the reactor and then the Monte Carlo (molecular-scale) part is employed. MC model thus uses the quantities pre-calculated by reactor-scale model: temperature, concentration of monomers in polymer/aqueous phase, concentration of radicals in aqueous phase and initiator concentration. The typical industrial recipe uses a combination of hydrophilic and hydrophobic comonomers, so the MC model can describe: (i) copolymerization only in polymer particles, (ii) copolymerization only in aqueous phase, and (iii) combination of both previous models resulting in a complex MC simulation of hetero-phase multi-monomer copolymerization in both polymer particles and water.

The MC model simulates one polymer particle and a small volume of bulk aqueous phase in parallel (physical interaction between polymer particles is thus neglected). The

Monte Carlo simulation utilizes the so-called “competition technique” for the simulation of growth of polymer chains. In this approach, the elapsed time of the process is measured by the number of monomeric units added to the growing radicals by propagation. In each step of the algorithm, every kinetic event that can happen (listed below) is associated with the time (randomly generated with a given probability distribution) that elapses until the realization of that event. The event with the shortest time is then selected as the one that actually happens. In this way, propagation reaction (as the one, which happens most often) is eliminated from the algorithm and thus all radical(s) existing in the polymer particle can propagate by hundreds of units during one algorithm step, leading to the significant decrease in simulation time. An algorithm scheme, which shows how we can eliminate propagation with varying state variables, is in **Figure 1**.

Besides chain propagation, the following kinetic events are considered in the MC simulation in polymer particle:

- absorption/desorption of oligomeric radical from/to aqueous phase,
- radical termination by combination,
- chain transfer to monomer,
- chain transfer to polymer.

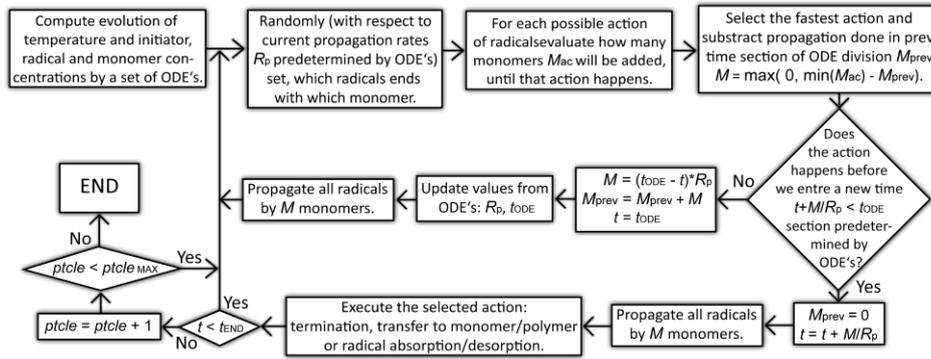


Figure 1: Algorithm scheme of hybrid MC approach.

We extended the basic competition model of Tobita (1995) to take into account arbitrary dosing profiles, copolymerization of two water-insoluble monomers and chain transfer to polymer creating the long chain branching. Intensive branching accompanied by chain termination by combination can lead to the formation of polymer gel. Presence of the polymer gel formally leads to the growth of weight-average molecular weight M_w *ad infinitum*, rendering the method of moments not applicable for these systems. Following the Tobita’s scheme (not computing propagation directly in the algorithm, but use precomputed concentration profiles from ODE), the model is precise and fast enough for on-line control.

The structure of MC algorithm describing the copolymerization in aqueous phase is very similar to the previous one, but in this case, we consider a constant control volume. The control volume has to be large enough so that we have at least two radicals in the aqueous system for most of the time. Only this way we can correctly estimate a time at which the termination by chain combination happens.

Besides chain propagation, MC considers following kinetic events in water phase:

- decomposition of the water-soluble initiator into radicals,
- chain termination by combination,
- chain transfer to monomer.

MC simulations of one or more polymer particles and aqueous phase were connected by following each radical on its way from the aqueous phase to the polymer particle (introduced via radical absorption rate k_a) and eventually on its way back (introduced via radical desorption rate k_d). We chose to neglect radical desorption, because we are considering systems with particle diameter above 100 nm, where radical desorption is not so common (Asua *et al.*, 1989). With this assumption, if radical enters the particle, it cannot desorb again, so one particle is isolated from others, it can be computed separately, and the algorithm can be fully parallelized.

Simulation of four particles (each containing around 40,000 chains, so that statistical sample is sufficient) in parallel in MATLAB environment on standard desktop PC takes around 13 s for the whole process in aqueous and organic phases.

3. Results and Discussion

Deterministic part of the model predicts conversion of all four monomers in agreement with provided experimental data (**Figure 2**). Comparison of product molecular weight distribution predicted by hybrid MC model and experimentally characterized by GPC-SEC is presented in **Figure 3**.

In experimental data for MWD (**Figure 3a**), we can observe a distinguishable peak for small molecular weights, which is slightly underestimated by the model. We believe that this small peak represents polymer chains born in aqueous phase, because the relative ratio compared to the second peak corresponds to the monomer feeding data. However, if we artificially increase the number of chains born in aqueous phase, we obtained a bimodal distribution, having the peak corresponding to the smaller molecular weights too large (**Figure 3b**). In linear free radical polymerization without a chain transfer agent (as is the case in aqueous phase), we can theoretically reach polydispersity index between 1.5 (when dominant reaction besides propagation is termination by combination) and 2 (when dominant is termination by disproportionation or transfer to monomer), but the peak from experimental data has much smaller polydispersity. Therefore, for future improvement we suggest to make the rate of radical absorption to polymer particles rate dependent on the radical length in a way that the larger radicals are absorbed faster (as also presented in Hamzehlou *et al.* 2014). Thus, larger polymer chains would enter the polymer particles and grow there even further. With this modification, we might achieve the desired small peak in the full distribution.

A more complex behaviour of the radical absorption rate is implied also by faster conversion growth of the water-soluble monomers (monomers 3 and 4) at the end of the polymerisation process (after the monomer feeding is stopped – last experimental points, **Figure 2**). When hydrophobic monomers (1 and 2) are depleted, the decomposed water-soluble initiator should not enter the polymer particles as frequently as when the hydrophobic monomers are present in the system.

Monte Carlo model for the aqueous phase shows a slight discrepancy in weight-average molecular weight M_w compared to the deterministic model based on polymer moments

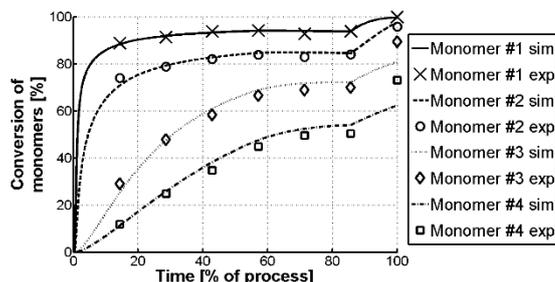


Figure 2: Comparison of predicted and measured conversion of both hydrophobic (1, 2) and hydrophilic (3, 4) monomers during the reaction. Experimental data come from the lab-scale reactor at BASF.

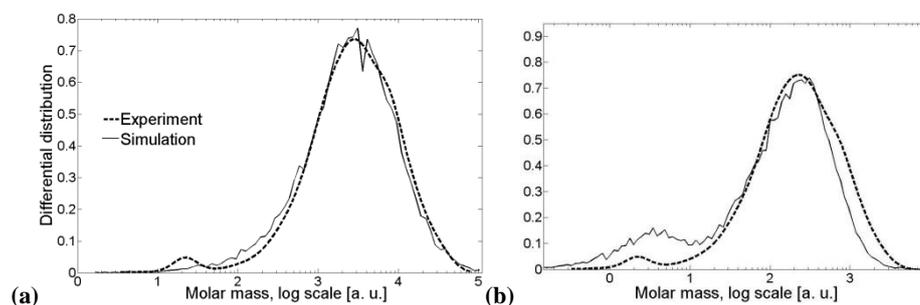


Figure 3: Comparison of measured and predicted molecular weight distribution of copolymer product for (a) the original model settings, and for (b) the model with artificially increased number of polymer chains formed in aqueous phase.

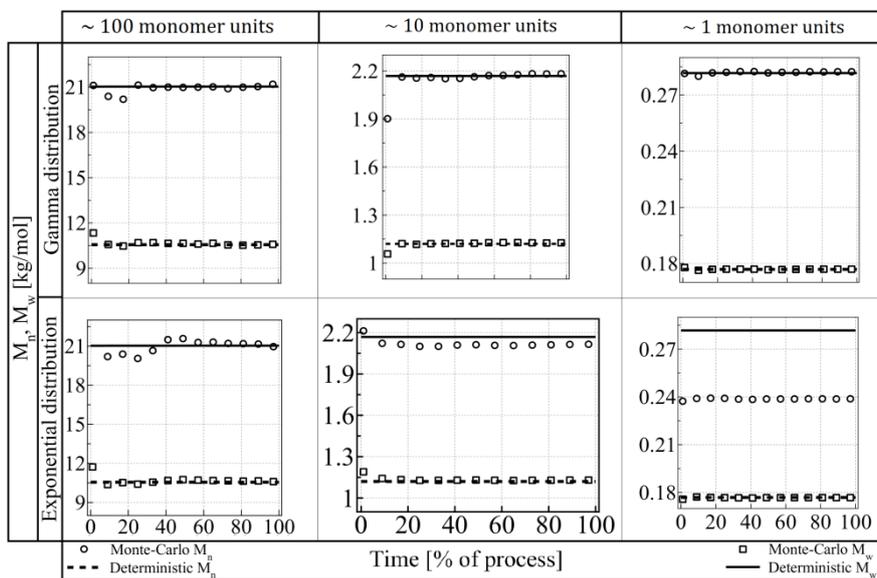


Figure 4: Average molecular weights of water-born polymer chains predicted by the method of moments (“process model”, lines) and Monte Carlo simulation (symbols) using different distributions of random numbers.

(**Figure 4**). At studied conditions, the average length of polymer chains in the aqueous phase is in the order of only 10 monomer units. For such short chains, random numbers generated with exponential distribution (usually used in MC simulations) have inappropriate variance. Using other, *e.g.* gamma, distribution (**Figure 4**) is unacceptable for MPC, because it slows down the calculation. Moreover, aqueous phase has a continuous character, so it is more reasonable to use continuous model for aqueous phase in MPC. Nevertheless, for a multiphase system, hybrid Monte Carlo simulation provides extended predictions within several seconds, so it is more suitable for MPC.

4. Conclusions

To the best of our knowledge, we are the first to report a successful implementation of a mathematical model for such a complex model, as two-phase four-monomer emulsion copolymerisation, based on hybrid Monte Carlo approach, which is fast enough for MPC. Our model provides multiple predictions: conversion of individual monomers, full MWD, average particle size, branching density, copolymer composition and its detailed molecular architecture. Both conversions and MWD of the copolymer are predicted in a reasonable agreement with experimental data. We demonstrated why ODE-based models (usually employed in MPC) are not suitable for emulsion copolymerisation, where transfer to polymer takes place. The developed model is fast enough – computation takes several seconds on standard desktop PC in MATLAB environment. Therefore, it will be employed for online model-based predictive control (MPC) and optimization of the industrial pilot-scale reactor. For that purpose, it will be necessary to reliably evaluate statistical error, which is inherently present in the outputs of stochastic models, and estimate computational time before the computation itself, so the process controller will be prevented from freezing.

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