

Modeling of High-Pressure Processes for Homo-, Co-, and Terpolymerization

Lukas Bender, Paul Peikert

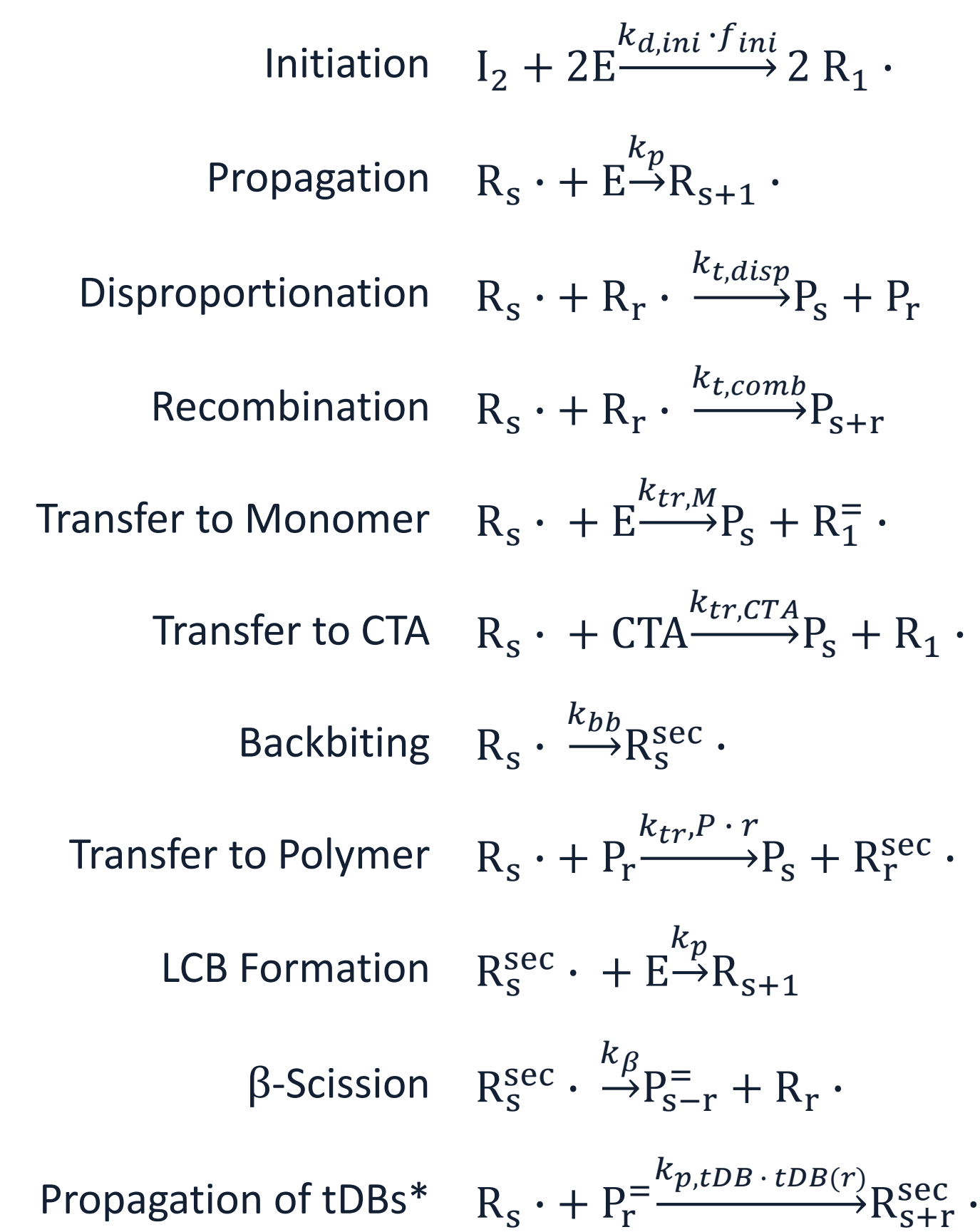
Department of Chemical Engineering, College of Liberal Arts and Sciences, University of Illinois at Urbana-Champaign

Introduction

This research explores the modeling and simulation of the high-pressure processes of ethene homopolymerization, ethene-propylene copolymerization, and ethene-vinyl acetate-propylene terpolymerization, all based upon empirical data from an autoclave mini-plant. Simulation aided product design is frequently applied to describe the high-pressure process of ethene polymerization and its comonomers. These simulations allow for the prediction of large scale changes of polymer properties with a chosen set of initial process conditions.

Ethene Polymerization Basics

The polymerization of ethene follows the below reactions. The modeling however only considers all of the reactions except the propagation of terminal double bonds (tDB).



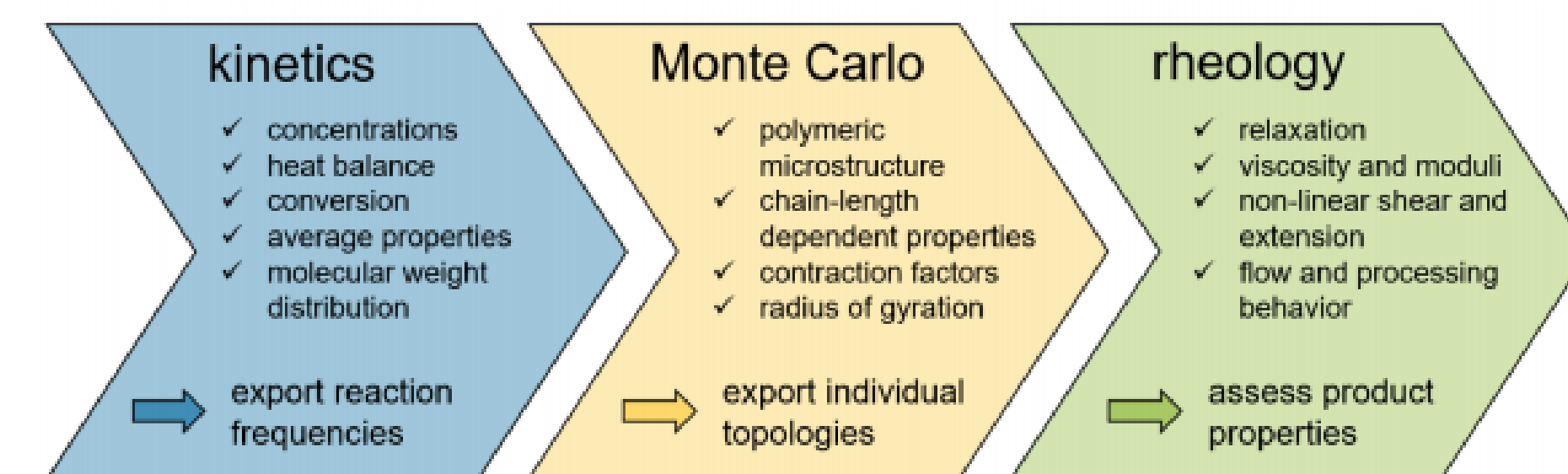
Motivation

The working group Busch utilizes a relationship between the melt flow rate (MFR) and the average change length of a polymer (Mn) given by an industry partner based upon empirical data. MFR is the mass flow rate of a melted thermoplastic under a desired pressure in 10 minutes.

$$MFR = f(Mn) \quad (1)$$

When applied to the high-pressure polymerization of ethene in our mini-plant, the relation deviates. This deviation can be explored through the use of a rheological simulation of the polymerization process.

Simulation Methods



This research uses a three-step modeling technique, which includes deterministic modeling of kinetics, stochastic modeling of microstructure, and rheology modeling of flow behavior. Among other properties, the deterministic modeling outputs reaction frequencies. The stochastic models calculate probabilities of reaction paths from these reaction frequencies, and output the topology of individual macromolecules. From this topology a rheology model can then calculate properties such as relaxation, viscosity, and processability. This work only explores deterministic and stochastic modeling. The benefit of this approach comes from the multiple validation of each step. Each step may model the distribution of the average chain length, which is compared to the experimentally determined distribution for validation.

Kinetics Simulation with Predici

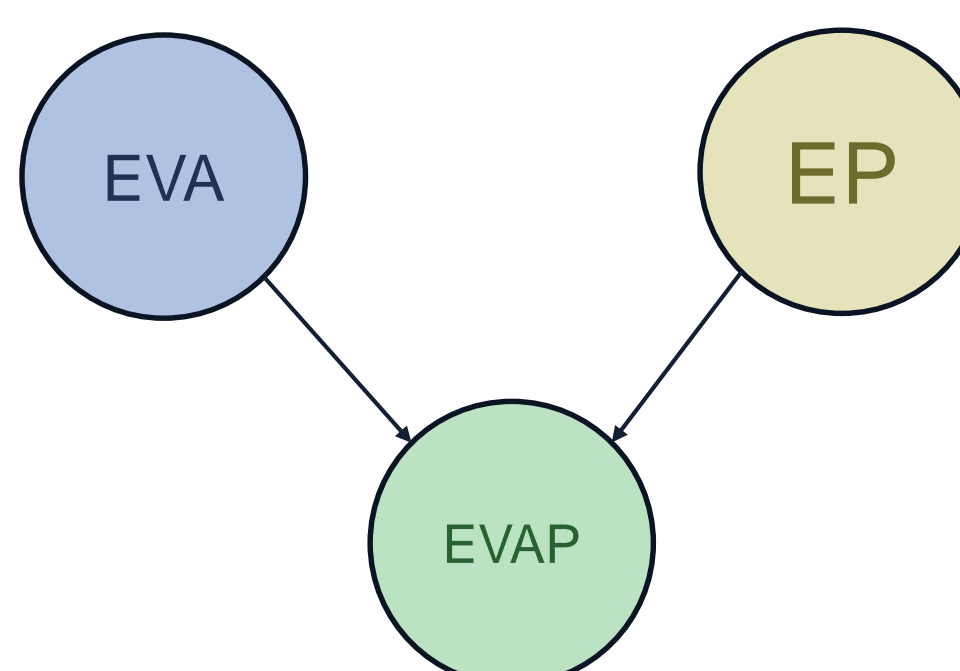
Predici 7 (Polyreaction Distribution by Countable System Integration) is used to model the homopolymerization of ethene, the copolymerization of ethene and propylene, and the terpolymerization of ethene, vinyl acetate, and propylene (EVAP).

Stochastic Stimulation with Monte Carlo

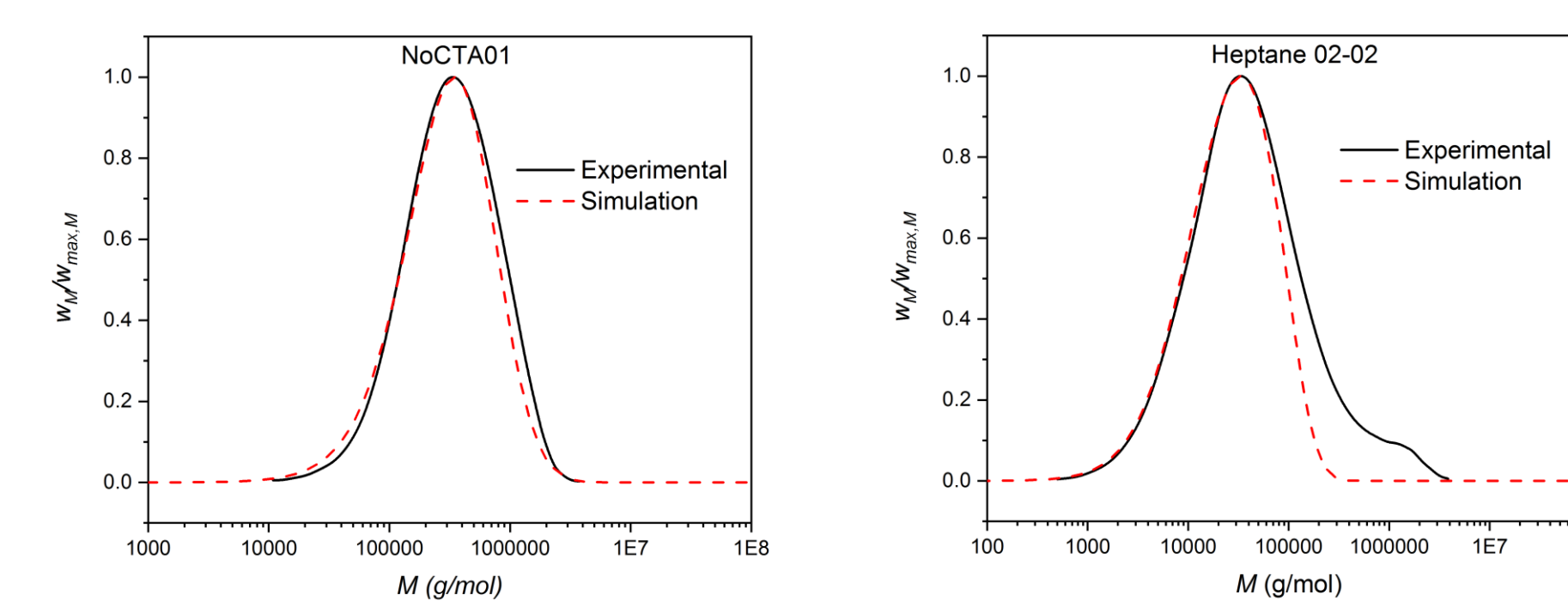
A hybrid Monte Carlo model is used to simulate the microstructure of the homopolymerization of ethene. The Monte Carlo transforms the reaction frequencies outputted by the Predici model. While the simulation iterates over time steps, incrementing a molecule's residence position. For every time step, the found probabilities are compared against random numbers to simulate these reactions.

Terpolymerization Method

This research attempts to create a model to simulate the terpolymerization of EVAP. To achieve this, a model of ethene-vinyl acetate (EVA) copolymerization was combined with another model of ethene-propylene (EP).



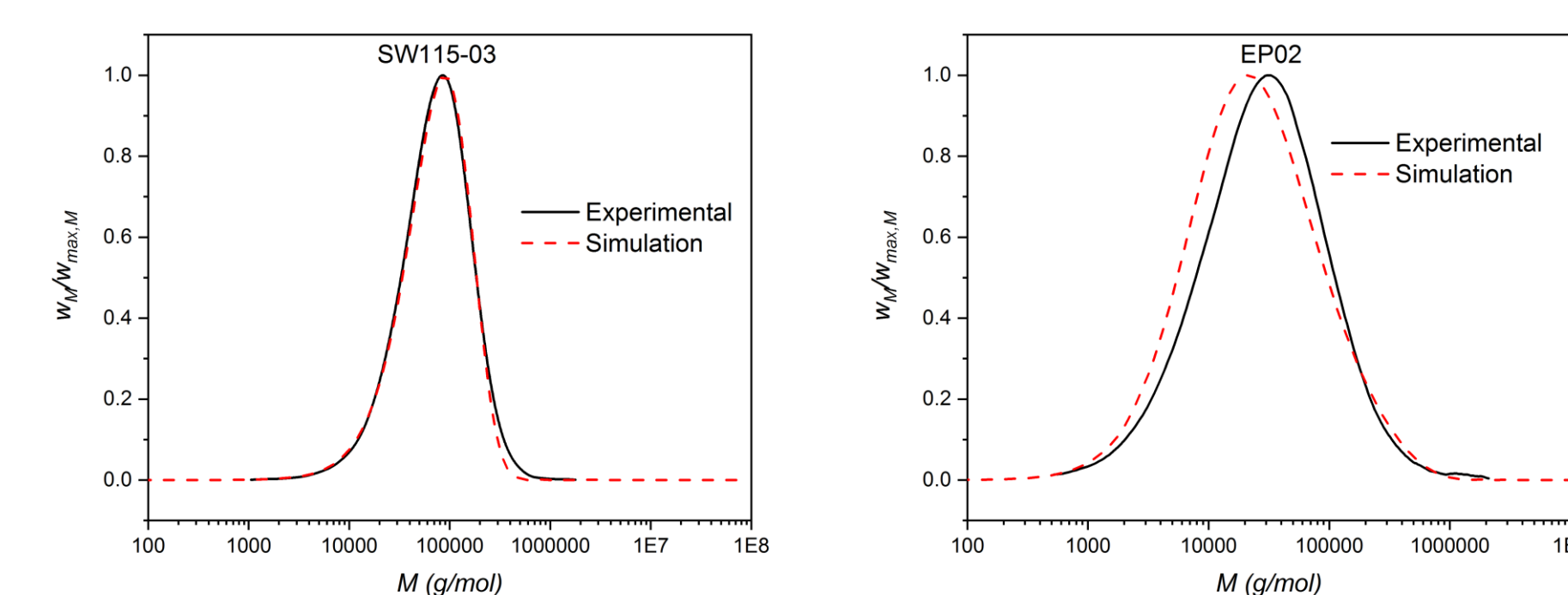
Results



The numerical homopolymerization of ethene simulation is broken into five experiments with heptane as a chain transfer agent (CTA) and three without CTA. The above figures are one experiment out of these two sets, with NoCTA01 the polymerization with no CTA and Heptane 02-02 with heptane CTA. The simulation Mn distribution fits nicely to the experimental distribution, where the peak width is in the same shape and the peak maximum in the correct position. The simulation with heptane CTA doesn't fit exactly in higher chain lengths because of fouling effect from an older version of the mini-plant. These are not seen in the experimental without CTA because the mini-plant was updated to fix this issue.

Number of Molecules	Heptane-01 Mn	Heptane-02 Mn	Heptane-03 Mn	Heptane-04 Mn	Heptane-05 Mn
Predici	10098	12717	13658	16730	18628
500000	10409	12108	13065	15971	18025
1000000	10376	12151	13065	16140	18275
Error in %*	2.75	4.45	4.34	3.52	1.89

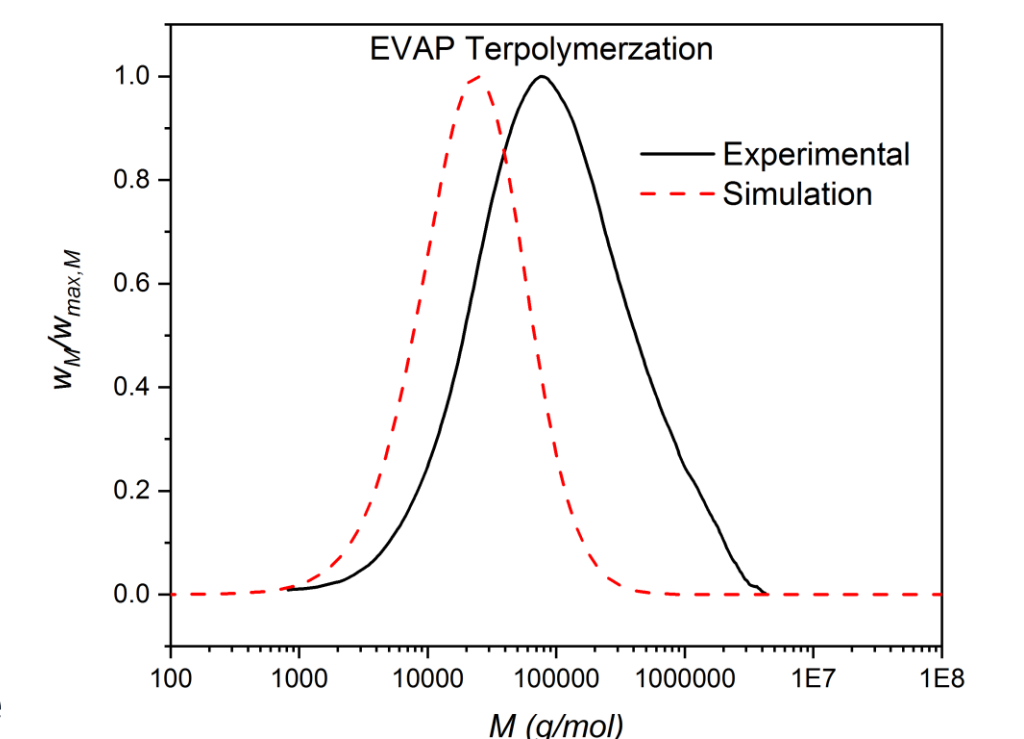
The stochastic ethene homopolymerization simulation achieves good results with a low error when comparing Predici found Mn with the simulation at one million molecules and with increasing molecules the deviation becomes smaller. However this deviation is still too high to move onto a rheological simulation. This deviation stems from the Monte Carlo model which handles back biting differently than Predici.



The numerical ethene-propylene copolymerization simulation is broken into fifteen total experiments, ten with low conversion and five relatively high conversion. The two above figures are one experiment from these sets with SW115-03 from low conversion and EP02 from high conversion. The rest of the experiments in each set look identical to the above figures from their respective sets. The low conversion simulation fits the experimental Mn distribution well. The high conversion simulation has a left rotation deviation of the peak, which is also seen in the other high conversion simulations.

Results

The numerical terpolymerization simulation was built and tested with one experiment. The simulation distribution is shifted to the lower chain lengths. To determine the source of this issue, the simulation may run as a copolymerization of two of the comonomers by setting a monomer flow rate to zero. From doing so, a shift can still be seen in the copolymerization of ethene and propylene, but not for ethene and vinyl acetate. This deviation stems from the difference in modeling of the two copolymerization processes. An assumption is made that the radical on a propylene unit acts the same as one on an ethene unit, which in turns means that some of the reaction coefficients of ethene and propylene are identical. This assumption may not hold and the stabilization of a tertiary radical may retard these reactions with a propylene unit. This is also related to the deviation seen in the previous EP high conversion model.



Conclusions

Progress toward evaluating the deviation of an industry partner's correlation between chain length and melt flow rate was made with the successful development of numerical and stochastic simulations of the high-pressure process of ethene homopolymerization. Progress toward developing a copolymerization and terpolymerization model of ethene-propylene and ethene-vinyl acetate-propylene was made and challenged previous assumptions. In the future, these models will be used to continue evaluating high-pressure polymerization processes.

Acknowledgements

I wish to give thanks to my supervisor Paul Peikert and the Busch working group from the Technical University of Darmstadt for taking me on as an intern and allowing me to take part in their research. Thanks to them have able to explore much about the polymerization aspect of chemical engineering.



TECHNISCHE
UNIVERSITÄT
DARMSTADT

ILLINOIS