

WALL LAYER FORMATION IN CONTINUOUSLY OPERATED TUBULAR REACTORS FOR FREE-RADICAL POLYMERIZATIONS

Stefan Welzel, University of Stuttgart
stefan.welzel@icvt.uni-stuttgart.de
Prof. Ulrich Niekén, University of Stuttgart

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Specialty polymers such as Polyvinylpyrrolidone (PVP) are mainly produced in batch or semi-batch operated tank reactors due to its flexibility and robustness. Continuous reactor systems have been considered as alternative for process intensification to increase energy efficiency and maintain flexibility. Especially, tubular reactors with mixing elements are of interest to manage low-volume products and to ensure good heat transfer. A serious problem of continuous operation in mixer-reactors is the formation of fouling deposits which can result in blocking of continuous reactors.

A prerequisite to formation of fouling deposits and wall layers are side reactions which produce high molecular weight, branched, or even crosslinked polymer chains. [1] The formation of these polymers (gel formation) occurs preferably in dead zones behind mixing elements as well as close to the wall. The locally increased residence time in such regions increase the impact of side reactions. Formation of a viscous layer at reactor walls or dead zones changes the flow pattern, leads to large cross-sectional concentration gradients and amplifies diffusive mass transport of monomer. Since large and branched polymer chains remain longer in the viscous regions due to the low diffusion rate, a highly viscous layer is formed. Such behavior has been reported for polymerization in tubular reactors, for example [2], [3].

The polymerization kinetic of N-vinylpyrrolidone (NVP) has been extended by side reactions. Formation of terminal double bounds and subsequent branching points was identified as the cause of high molecular, branched polymer [1]. To investigate the interplay between hydrodynamics, diffusive mass transport and reaction kinetics we conducted CFD simulations in tubular reactors without mixing elements and carefully compared model predictions to a comprehensive set of experiments. The polymer properties are represented by their moments. To model the transport equations for the moments, the low mobility of the polymer chains compared to the monomer and solvent must be considered. Therefore, a new approach based on Maxwell-Stefan diffusion was derived, which allows to formulate transport equations for polymer moments. The model has been implemented into the open-source package Openfoam®. CFD simulations predict the formation of a highly viscous wall layer in a tubular reactor, which strongly depends on monomer and initiator concentration. To validate model predictions a capillary reactor was set up and the residence time distribution of experiments and CFD predictions were compared. To determine the residence time experimentally, a salt solution was used as a tracer and measured with a conductivity cell at the inlet and outlet of the reactor. Different experiments with varying monomer and initiator concentrations are carried out to validate the model predictions in a wide range of conditions.

An example of a CFD simulation is shown in Figure 1, which presents the polymer weight fraction for a feed monomer weight fraction of $w_M = 20\%$ after 100min reaction time. The formation of wall deposits changes the shape of the residence time distribution. The viscous layer leads to a faster breakthrough of the tracer impulse and a strongly increased tailing, which is in accordance with experimental findings.

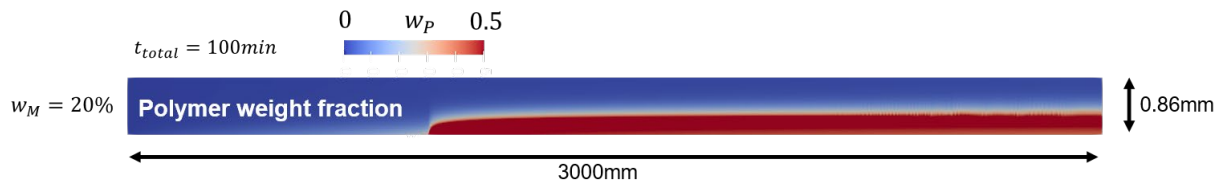


Figure 1: Polymer weight fraction for different monomer feed concentrations after 100min of reaction time.

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