

# Calorimetry & Simulation: Heat Balance of Anionic Polymerization in Batch Reactors

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## Introduction

Polymers are an essential product of the chemical industry and an ever-present material in our daily lives. The production of polymers comes with several challenges. The challenges are not only in terms of the successful accomplishment of the synthesis that incorporates the correct formulation of the reaction that high conversion of the monomers to polymers and all the other factors but also challenges with regard to safety-related issues. The reason for this lies in the exothermic nature of nearly all industrially important polymerizations [1], regardless of the underlying reaction mechanism. Because of this behavior, calorimetric measurements are a central part of the development of polymerization processes. In addition to experimental measurements, simulations can help in the thermal design of polymerizations.

The software package PREDICI developed by Michael Wulkow [2] is specialized on the kinetic modeling of polymerization reactions. The focus of this software package lies in the simulation of the polymer synthesis, and especially on the molecular properties such as the molecular weight and the molecular weight distributions of the synthesized polymer. However, due to the implemented script-based language, it is possible to extend the models in order to describe further essential aspects of chemical processes (e.g. the heat balance). Such a model is presented here using the example of the anionic copolymerization of styrene and isoprene carried out in a batch process. The reason for that is that the heat balance is associated strongly with the safety of polymerization processes and provides essential information for the proper design of the large-scale synthesis process in a batch reactor.

## Model Structure

The kinetic of the anionic polymerization of styrene is represented by a simple model, which describes the steps of initiation, propagation, as well as the imposed deactivation step after the addition of a termination mean. The same model was further extended to cover the copolymerization with isoprene using rate constants and copolymerization parameters from the literature [3].

The heat balance of the reactor is modeled using two coupled balance spaces representing either the inner volume of the reactor as well as the tempering jacket. This modeling approach was first used to model a reflux calorimeter [4].

The balance equation with the heat accumulated inside the reactor volume ( $\dot{Q}_A$ ) includes the reaction heat ( $\dot{Q}_R$ ) and conductive heat flow ( $\dot{Q}_C$ ) through the reactor wall as described in equation (1).

$$\dot{Q}_A = \dot{Q}_C + \dot{Q}_R \quad (1)$$

with the overall heat transfer coefficient  $k$ , the heat exchange area  $A$ , the temperature in reactor  $T_R$ , the temperature in the jacket  $T_J$ , the reaction rate  $r$ , the volume  $V$  and the polymerization enthalpy  $\Delta H_p$ , as described in equations (2) and (3)

$$\dot{Q}_C = k \cdot A \cdot (T_R - T_J) \quad (2)$$

$$\dot{Q}_R = r \cdot V \cdot \Delta H_p \quad (3)$$

The model calculates the overall heat transfer coefficient ( $k$ ) from the individual jacket-sided ( $\alpha_J$ ) and reactor-sided ( $\alpha_R$ ) heat transfer coefficients. These are derived from their respective Nusselt Number ( $Nu$ ) using different empiric correlations following the equation (4).

$$\frac{1}{k} = \frac{1}{\alpha_R} + \frac{d_{wall}}{\lambda} + \frac{1}{\alpha_J} \quad (4)$$

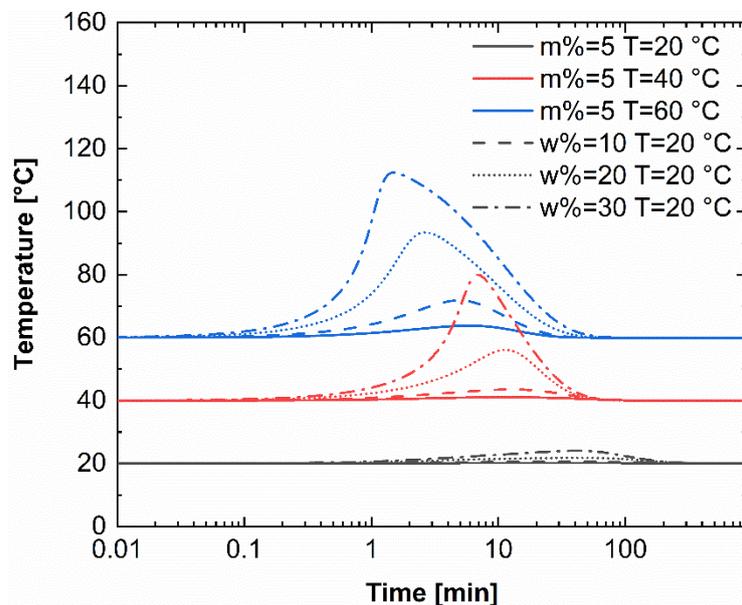
with the diameter of the reactor wall  $d_{Wall}$ , the thermal transmittance  $\lambda$  and a characteristic length  $L$  (equation 5).

$$\alpha = \frac{Nu \cdot \lambda}{L} \quad (5)$$

Due to this approach, the model can help investigate the influence of process parameters such as the reaction temperature, stirrer type, stirring speed or the temperature and flow rate inside the jacket on the thermal behavior of the process.

## Results

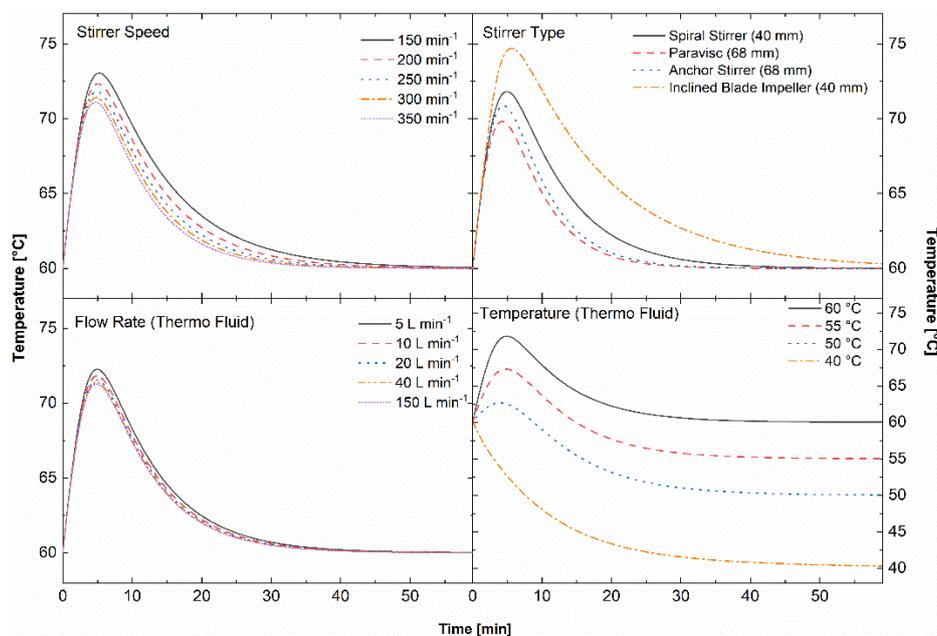
The model was first used to simulate polymerizations of styrene (Figure 1) with the use of *sec*-butyl lithium in cyclohexane as the solvent, carried out at different initiation temperatures (20 °C - 60 °C) and varying monomer content (5 wt% - 30 wt%).



**Figure 1:** Simulated polymerization with varied initiation temperature and monomer content.

The simulations show that the thermal behavior of the investigated polymerizations strongly depends on the synthesis recipe and initiation temperature. The risk of a thermal runaway can be evaluated based on the simulated temperature profiles using different criteria reported in the literature [5].

In the second set of simulations, one particular recipe (10 wt% monomer content at 60 °C) was used to investigate the influence of four process parameters (stirring speed, stirrer type and the volume flow rate as well as temperature in the jacket) on the temperature profiles of the reactions.



**Figure 2:** Simulated temperature profiles of a polymerization carried out with varied process parameters (stirrer speed, stirrer type, flow rate and temperature in the jacket).

The expansion of the simulation for the case of copolymerization of styrene and isoprene was the next step of the study. The observation of the process indicates that the same effect as in the case of the homopolymerization of styrene occurs. The temperature profiles however are strongly influenced by the process parameters as in the case of styrene homopolymerization.

Comparing the investigated process parameters, the temperature of the thermo-fluid has the most substantial influence on the temperature profiles. The results of these simulations were used to investigate further the thermal runaway risk associated with these reactions as well as the scale-up of the reactions from a 0.5 L to a 15 L scale. (submitted for publication) [6]. Reaction calorimetry is capable to enlighten further the polymerization process and to provide the correct experimental design. [7]

## Outlook: Simulation & Calorimetry

The model was successfully applied to simulate the anionic polymerization of styrene with different process parameters. Based on these data, the thermal behavior and runaway risk of these reactions can be evaluated. Until now, this study has been based exclusively on simulations and data from the literature. Reaction calorimetry is a valuable method for experimental validation. This allows important parameters such as the overall heat transfer coefficient to be determined and compared with the model's predictions. A model validated in this way, in combination with complementary calorimetric measurements, can contribute to faster, resource-efficient and safe process development and scale-up of polymerizations. The structure of the model also allows quick adaptation to further polymerizations if their kinetics are known.

Specifically, reaction calorimetry can provide a deep insight into the problem of thermal runaway. In the typical experimental laboratory setup, there is no way to obtain actual data for all the different recipes of the polymerization that lead to the thermal runaway process due to safety. With the use of reaction calorimetry, model experiments can be performed and the synthesis of polystyrene as well as of polystyrene-polyisoprene copolymer can be closely monitored near the limits of a dangerous situation in a safer manner. Critical parameters such as the stirring of the systems (stirrer type, stirring speed) that define the safe operation can be closely observed and in this way, a safer process can be designed.

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