MODELING AND CONTROL OF MOLECULAR WEIGHT DISTRIBUTION IN A LIQUID-PHASE POLYPROPYLENE REACTOR
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DISSERTATION

to obtain
the doctor’s degree at the University of Twente,
on the authority of the rector magnificus,
prof. dr. W. H. M. Zijm,
on account of the decision of the graduation committee,
to be publicly defended
on Thursday January 26th 2005 at 15:00

by

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This dissertation is approved by

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\textbf{Prof. dr. –Ing. habil. Günter Weickert} and \textbf{Prof. dr. ir. Brian Roffel}

and the assistant promoter
\textbf{Dr. ir. Ben Betlem}
Abstract

Polypropylene is widely used in many diverse applications. For different applications, different molecular weight distributions are required; consequently, accurate control of the polymerization process is a necessity.

If conditions can be controlled well, there is still another challenge, namely, optimal operation of the process during the transition from one polymer grade to another one. To find the optimal production policy, the use of model-based approaches is preferred. In these approaches, accurate models for kinetics and molecular properties play a crucial role.

This thesis is concerned mainly with two topics, firstly, the investigation of the aspects of liquid phase polymerization of propylene using a fourth generation Ziegler-Natta catalyst at conditions resembling those of industrial units. Using the results of the first part, control of the molecular weight distribution of polypropylene, produced in a continuous pilot plant reactor, is studied.

The first objective of this research is to improve the understanding of the kinetics of propylene polymerization and the molecular weight distribution of the produced polymer.

The initial work concentrates on determining the impact of excluding gas-liquid mass transfer limitations, i.e. using fully-filled reactor, on the polymerization rate. The experimental results show that the polymerization rate is higher in a fully-filled reactor than in a partially-filled reactor. Moreover, it is found that the polymerization rate increases with increasing polymerization temperature.

It is also found that in fully-filled reactors the rate could be accurately estimated from reactor pressure and temperature profiles during the polymerization reaction. This method is known as the dilatometric method and compares well to the isoperibolic calorimetry method. To the authors knowledge this is the first time that the dilatometric method is used to estimate the polymerization rate for liquid-pool polymerizations.

Kinetic experiments were performed at different temperatures (60°C – 80°C) and hydrogen concentrations (0 – 27 mmol/mol) to determine the effect of the latter parameters on the polymerization kinetics. The results showed that the polymerization rate increases rapidly with increasing hydrogen concentration reaching a constant value at concentrations above 1.4 mmol/mol. However, at high hydrogen concentration, greater than 19 mmol/mol, the polymerization rate decreases. In addition, it was found that the polymerization rate increases with increasing temperature with approximately constant activation energy.
Additionally, a clear dependency is noticed between the polymerization rate and the deactivation constant. As the polymerization rate increases, whatever the reason for this increase, the deactivation rate constant increases.

The experimental results were used to model the initial polymerization rate, using the dormant sites theory, as a function of hydrogen concentration and polymerization temperature. In addition, the deactivation constant was correlated as a function of the initial polymerization rate, temperature and hydrogen concentration. The comparison between the predictions of these models and the corresponding experimental results revealed that the developed models fit the experimental results well.

Polymer properties were analyzed using gel permeation chromatography yielding a complete set of molecular weight distribution curves. The dependency of the average molecular weight on the hydrogen concentration was investigated using a Natta model, Mayo equation, and a model which was derived using the dormant site theory. The comparison revealed that the best description for the experimental data was obtained using the dormant site-based model.

The deconvolution of the molecular weight distribution curves resulted in a set of parameters, called termination probabilities, which were modeled as a function of the hydrogen concentration. The use of these parameters assisted in describing the entire distribution by a simple algebraic model.

The second objective of this research was to develop an accurate model for the propylene polymerization process. The model consisted of mass, partial mass, energy and volumetric flow balances. In addition, the model contained equations for the polymerization kinetics and polymer molecular weight distribution, which were previously developed in the kinetic study.

The third objective of this work was to develop a model-based control strategy for control of polymerization reactors. This controller was similar to generic model control; however, the integral action, which is used in GMC applications, was omitted. The model was updated on-line using measurements of the process-model mismatch. The updating scheme improves the model estimations for the delayed process measurements. The developed controller was able to achieve varying process goals during a product grade change and regulatory control. The performance of the developed control scheme was only superior when the interactions between process inputs and outputs were large.

The fourth objective of this study was the development of grade-change strategies. This was performed using the developed detailed model. Using the control parameterization technique, optimal manipulated variable profiles were determined for
hydrogen and catalyst feed rates. These trajectories were used to control monomer conversion and the entire molecular weight distribution of the produced polymer.

Pontryagin’s Minimum Principle is subsequently used with a simplified model to compute the optimal trajectories. Results of this approach were similar to the results from the optimization study using the detailed model.

The grade-transition was also performed using the nonlinear controller which was developed earlier in this thesis. It appeared that the model-based controller was also effective in realizing optimal grade changes.

The fifth objective of this research was to study the broadening of molecular weight distribution by operating the reactor under square wave perturbations in hydrogen and catalyst feed rates. Results were promising provided hydrogen could be removed from the reactor at a fast rate. In that case, a maximum increase in polydispersity index of a factor of two could be realized.
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