MODELING OF α -OLEFIN COPOLYMERIZATION WITH CHAIN SHUTTLING CHEMISTRY USING DUAL CATALYSTS IN STIRRED TANK REACTORS

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Summary

We report a kinetic model of chain shuttling copolymerization using dual catalysts for solution α -olefin polymerization processes. This model focuses on predicting polymer properties such as molecular weight and its distribution. We first validate the model through qualitative comparison between the model predictions and experimental observations¹ in a semi-batch and a CSTR. Examples are given to illustrate how the model can be used to examine the effects of chain shuttling rate constant and chain shuttling agent feed rate in a CSTR. Moreover, simulations demonstrate how to prepare polymers with desired properties through manipulating catalyst and monomer compositions in the feed.

Keywords

Kinetic and Reactor Modeling, Chain Shuttling Polymerization, Dual Catalysts, Polyethylene

Introduction

The discovery of chain shuttling polymerization opened up a new frontier for the production of novel olefin block copolymers (OBCs). The essence of chain shuttling polymerization is to introduce a chain shuttling agent (CSA) to reversibly transfer back the polymer chains to the catalyst while ultimately allowing the polymer chains to experience further growth. In the presence of two catalysts in a single reactor, each having varying abilities in incorporating comonomer, chain shuttling polymerization has been able to prepare OBCs. То achieve rapid commercialization of chain shuttling polymerization, a top priority was to develop kinetic and models that could accelerate reactor the commercialization. In this report, we describe a comprehensive kinetic model for the chain shuttling polymerization and then apply the model to reactor results to investigate key developmental questions.

Kinetic and Reactor Model

We consider a representative kinetic scheme including key reactions involved in solution α -olefin polymerization in the presence of CSA. Using the method of moments², we develop a kinetic model to keep track of the leading moments of the various types of polymer chains existing in the system. These moments are further reduced to polymer chain properties such as molecular weight and its distributions. Additionally, this kinetic scheme is incorporated to a fully mixed tank reactor model to simulate batch, semi-batch and continuous stirred tank reactors.

Model Validation

Arriola et al.¹ show that using dual catalysts alone in a semi-batch reactor leads to polymers with broad MWDs ($M_w/M_n = 13.6$) while adding CSA (diethylzinc) leads to polymers with narrow MWDs ($M_w/M_n = 1.33$). Moreover, carrying out chain shuttling polymerization using dual catalysts in a CSTR leads to polymers with narrow distributions ($M_w/M_n = 2$) while using dual catalysts alone results in polymers having broad MWDs ($M_w/M_n = 13.8$). We have utilized both semi-batch and CSTR models to simulate polymerization using dual catalysts in the absence and the presence of CSA. Our simulations shown in Figure 1 are consistent with the observations in the experiments as shown in Arriola et al.¹

Results and Discussions

Effect of Chain Shuttling Rate Constant in a CSTR

Successful chain shuttling requires that a CSA has the ability to shuttle between growing chains attached to different active centers. Manipulation of the chain shuttling rate constant in a CSTR model allows examination of the effect of chain shuttling rate constant on polymer chain architectures. As the chain shuttling rate constant increases, M_w/M_n approaches 2. When the chain

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shuttling rate constant is small, increasing the chain shuttling rate constant decreases M_n slightly. However, when the chain shuttling rate constant is sufficiently large, increasing the chain shuttling rate constant has no effect on M_n when hydrogen and CSA feed rates are constant. When the chain shuttling rate constant is increased too much, M_n actually increases as the active center compositions change.

Effect of Virgin CSA Feed Rate in a CSTR

Once an appropriate CSA is identified, the CSA feed rate can be manipulated to control the degree of chain shuttling and thus polymer chain architecture in a CSTR. In our model, we have assumed that CSA does not affect the intrinsic propagation rate constants for each catalyst and that changing CSA feed rate has no effect on bulk polymer composition, block copolymer composition, weight fraction of each block, overall mass conversion and fraction conversion of ethylene and octene. However, it does have an effect on molecular weight and its distribution. Increasing CSA feed rate leads to the decrease of both M_w and M_n . Additionally, M_w/M_n of the resulting polymers becomes smaller, approaching 2 at the limit.

Effect of Catalyst Composition in the Presence of Significant Chain Shuttling

Catalyst composition in the feed is another important variable that can be manipulated to tune molecular chain architectures. The effect of catalyst composition on bulk polymer composition and block copolymer composition are examined by increasing the molar fraction of catalyst 1 (soft catalyst). Even though increasing the molar fraction of catalyst 1 leads to an increase in overall octene content in the bulk polymer, the molar fraction of octene in soft block actually decreases. Close examination shows that increasing the molar fraction of catalyst 1 in the catalyst feed leads to the increase of octene conversion and a slight drop of ethylene conversion. Thus, the molar fraction of octene in the reactor drops. By increasing the relative amount of catalyst 1, an increase of weight fraction of block 1 originating from catalyst 1 is achieved. Furthermore, M_n increases significantly as the molar fraction of catalyst 1 increases while polydispersities of the resulting polymers are around 2 for a wide range of catalyst compositions.

Effect of Monomer Composition in the Feed in the Presence of Chain Shuttling

Certain effects on product properties are predicted by the model when monomer weight composition is varied in the feed. As the ethylene weight fraction in the feed increases, the molar fractions of ethylene in both the bulk polymer and each block increase while the weight fraction of hard blocks in the bulk polymer remains nearly flat. Moreover, the overall mass conversion as well as the fractional conversions of ethylene and octene increase when the ethylene weight fraction in the feed increases because the relative reduction in the less reactive octene tends to accelerate polymerization. It has also been shown that changing ethylene weight fraction in the feed leads to the variation of polymer properties such as M_n . While the average chain length changes, the polydispersities remain around 2 because of chain shuttling. Model predictions show that monomer feed composition is also a variable that can be used to tune block properties.

Conclusions

A model for chain shuttling copolymerization using dual catalysts has been developed in this study. Validation of the model has been carried out against experimental observations qualitatively. Simulations demonstrate how this model can be employed for improved process development and operation. Model predictions show that operating a chain shuttling copolymerization in a CSTR leads to the production of unique olefin block copolymers with control of such characteristics as molecular weight and its distribution, copolymer composition, and block composition. Selection of a CSA with appropriate chain shuttling rate constants is also important to control molecular weight distribution. Moreover, the model has been used to analyze the effects of catalyst composition in the feed and feed rate of chain shuttling agent.

References

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Figure 1. Evolution of polymer properties such as M_n and M_w/M_n in the semi-batch reactor in the absence and in the presence of CSA.