KINETIC MODELING AND PARAMETER ESTIMATION OF SLURRY PROPYLENE HOMOPOLYMERIZATION USING Rac-Et[Ind]$_2$ZrCl$_2$/MAO

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Abstract

Development of single site catalyst technology represents one of the most important innovations in the last decade for the polymer industry. Nowadays, thermoplastic industries for polypropylene are mainly based on Ziegler-Natta catalysts. However, projections forecast substantial growth for metallocene-based polypropylene demand [1]. Metallocene catalysts are able to produce polymers in a very broad molecular weight range with a very narrow molecular weight distribution (MWD), and have the capability to control regio- and stereochemistries.

Olefin polymerization kinetics has been investigated for a wide variety of metallocene catalyst systems [2, 3, 4]. Most researchers agree that propagation occurs via a single type of active site. Controversy exists on the assumption that catalyst activation and chain initiation are extremely fast. Nevertheless, extensive data suggest that this assumption is valid only when the metallocene/methylaluminoxane (MAO) ratio is sufficiently large [5]. Some models include chain transfer reactions to monomer or MAO in which dead polymer chains are produced from growing chains [5, 6]. Chain termination reaction from which dead polymer is produced from actively growing chains is also present in most models [7].

We have developed a kinetic model for homopolymerization of propylene by Brintzinger's catalyst. As compared to previously designed models for metallocene catalyzed olefin polymerization, this newly developed model offers the following improvements: (1) removal of the assumption of instantaneous chain activation; (2) inclusion of a generic catalyst deactivation reaction to account for decreasing catalyst activity with time; and (3) inclusion of chain transfer reaction to monomer that can have a large effect on MWD.

Experimental data collection is needed to estimate the parameters (kinetic rate constants) of the kinetic model. For this purpose, slurry homopolymerization reactions of polypropylene catalyzed by single-site metallocene catalysts using MAO as cocatalyst were performed in a semi batch reaction system. Experiments using rac-ethylene-bis(1-indenyl)zirconium dichloride (rac-Et[Ind]$_2$ZrCl$_2$) were performed. This species, known as Brintzinger's catalyst, has a relatively low activity and produces isotactic polypropylene with infrequent regio-errors. Experiments were performed in order to determine the effect of process conditions; such as concentration of monomer, temperature and Zr/MAO ratio on the rate of reaction, and final properties of the polypropylene. Monomer flow rate to the reactor was measured continuously to determine the rate of reaction. Post-batch laboratory analysis techniques were used to characterize the product: average molecular weights and MWD were measured with high temperature GPC, nature of the end-groups is analyzed by ^{1}H NMR spectroscopy to identify chain transfer mechanisms, and ^{13}C NMR spectroscopy is used to analyze tacticity, stereo- and regio-errors.

Due to the nature of experimental data collection, the parameter estimation problem involves both on-line measurements and laboratory measurements performed at the end of the

batch. By this reason, estimation of parameters was accomplished into two sequential sub-problems: (1) chain initiation/propagation and catalyst deactivation parameters were estimated from on-line polymerization rate data, (2) chain transfer parameters were estimated from end-of-batch data obtained by high-temperature GPC and ^{1}H NMR spectroscopy. Both sub-problems were formulated as nonlinear optimization problems in which the kinetic rate constants were the decision variables. Least-squares method was used to minimize the difference between the experimental measurements and the model predictions. The minimization problem is subject to constrains imposed by the model equations. These constrains are a set of nonlinear algebraic equations approximated by applying temporal discretization techniques to the dynamic model.

The final goal of this research is to develop a predictive kinetic model that can be extensible to a number of metallocene catalyst systems. A predictive kinetic model would be able to determine reaction kinetics at experimental conditions, such as temperature or pressure, different from the one used to determine the parameters of the model. In the other hand, to make the model extensible to other metallocene catalyst systems, such as rac-ethylene-bis (4,7-dimethyl-1-indenyl) $ZrCl_2$; introduction of chemical reactions to account for the effects of regio-errors would be necessary.

References

1. K.B. Sinclair, "*Future trends in Polyolefin Materials".* Macromol. Symp. **2001**. 173: p. 237-261.
2. E. Ochoteco, M. Vecino, M. Montes, J. C. de la Cal, "*Kinetic and Properties in Metallocene Catalysed Propene Polymerisations.*" Chem. Eng. Sci. **2001**, 56: p. 4169-4179.
3. T.S. Wester, H. Johnsen, P. Kittilsen, E. Rytter, "*The Effect of Temperature on the Polymerization of Propene with Dimethylsilylbis(1-idenyl)zirconium dichloride/Methylaluminoxane and Dimethylsilylbis(2-methyl-1-idenyl)zirconium dichloride/Methylaluminoxane. Modeling of kinetics*". Macromol. Chem. Phys. **1998**, 199: p. 1989—2004.
4. K. Thorshaug, J. A. Stovneng, R. Rytter, M. Ystenes, "*Termination, Isomerization, and Propagation Reactions during Ethene Polymerization Catalyzed by Cp2Zr-R+ and Cp*2Zr-R+. An Experimental and Theoretical Investigation.*" Macromolecules **1998**, 31: p. 7149-7165.
5. J. Huang, G.L. Rempel, "*Kinetic Study of Propylene Polymerization using $Et(H_4Ind)_2ZrCl_2/MAO$".* Ind. Eng. Chem. Res. **1997**. 36(4): p. 1151-1157.
6. J.M. Vela-Estrada, A.E. Hamielec, "*Modelling of Ethylene Polymerization with Cp_2ZrCl_2/MAO Catalyst*". Polymer, **1994**. 35(4): p. 808-818.
7. C. Yuan, D. Yan, "*Influence of termination and transfer on MWD of polymers: 9. Chain transfer to monomer and spontaneous transfer".* Polymer, **1988**. 29: p. 924-928.