ABSTRACT

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Title: Development of Quantitative Kinetic Models for Single-Site Olefin Polymerization
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A model-based approach was employed to reveal the elementary steps and the corresponding rate constants for the coordination polymerization of alpha-olefins catalyzed by post-metallocene single-site catalysts. A rich set of multi-response data including monomer consumption, molecular weight distribution, end-group analysis and chemical composition distribution were quantitatively analyzed in order to robustly determine the elementary steps and rate constants using specially designed software.

The traditional set of steps in the Cossee-Arlman olefin polymerization mechanism include initiation, propagation (1,2 insertion), mis-insertion (2,1 insertion), chain transfer and catalyst degradation. Using the quantitative kinetic modeling tools the reaction order of these steps and the associated rate constants were determined for a series of Zr[2-X-4-^{t}Bu-ONNO] (X=Me, Et, ^{i}Pr and ^{t}Bu) catalysts, where the size of ligand was varied. It was revealed that the catalyst can reversibly isomerize into dormant form, where the isomerization rate constant is greater with smaller ligands and polar solvent. Using the same quantitative modeling tools with multi-response data, the polymerization of 1-hexene via a Zr[tBu-ON^{NEt2}O]Bn_2 catalyst system was studied. It was determined that the catalyst has two different activated forms (one that produces oligomers and a second that polymerizes the oligomers), where their interaction results in branched polymer. Finally, a commercial ethylene oligomerization catalyst was studied, where it was determined that a reversible incorporation and a catalyst degradation are present in addition to metallacycle pathway.

Finally, the modeling tools were expanded to include copolymerization, where additional cross reactions between the two monomers were added to the elementary reactions in the Cossee-Arlman mechanism. Typical copolymerization experimental data were simulated, where the simulated data

was then analyzed to determine if the underlying kinetic mechanism could be recovered from the simulated data. It was shown that by appropriate choice of experimental conditions it is possible to determine both the form of the kinetic mechanism and the associated rate constants from experimental data. Of particular significant was the use of the RI signal in the GPC analysis of molecular weight, where the refractive index of ethylene in the polymer chain is significantly different than an α-olefin that has been incorporated into the polymer.