Practical, Information-Rich Kinetic Methods for Understanding Catalytic Alkene Polymerization

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Abstract

Knowledge of the time-resolved concentrations of active sites opens the door to more detailed understanding of catalytic processes. The chromophore-quench labeling method enables the determination of active site counts in polymerization reactions. Critical attributes of the method include high sensitivity (micromolar and lower catalyst concentrations), simplicity of detection (GPC analysis with a UV detector), and selective reactivity (the quench may be designed to react only with Hf, Zr, and Ti alkyls in the presence of Zn and Al-alkyls). Unlike poisoning based approaches, the quench-label method provides a positive output, with each actively propagating center producing a labeled polymer and, hence, a detector signal. Because detection is linked to GPC analysis, quench-labeling yields more than active site counts—the mass distribution of polymers attached to propagating centers at the time of quench, also, are revealed. The kinetic information embedded in the time-evolution of bulk and catalyst-bound polymer mass distributions dramatically increase the information-content, and decrease the number of experiments, needed for detailed kinetic analysis.

Applications of the quench-chromophore method to several homogeneous polymerization catalysts are used to illustrate unique insights into the workings of catalytic alkene polymerization. These applications include quantitative kinetic modeling, polymerization in the presence of chain transfer agents, copolymerization, catalysts that feature unusual rate profiles, and determination of the fundamental activation parameters associated with initiation, propagation, β-hydride elimination, and chain transfer with aluminum and zinc alkyls. Prospects for achieving detailed kinetic analyses under truly industrial conditions will be presented.