Kinetics and Mechanisms in Olefin Polymerization viewed by Real-Time NMR using Dissolution Dynamic Nuclear Polarization

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Because of its unrivaled capability to elucidate chemical structure in the liquid state, nuclear magnetic resonance spectroscopy has long been a method of choice to determine catalytic mechanisms in polymer science. Primary limitations of NMR spectroscopy in this context include a low sensitivity compared to other methods such as optical spectroscopy, concomitant with a typical requirement for the use of isotope labeled compounds. In this presentation, the application of dissolution dynamic nuclear polarization (D-DNP) will be described to overcome some of these limitations for the study of olefin polymerization reactions. D-DNP is a hyperpolarization technology capable of enhancing the liquid state NMR signal in a single scan by several orders of magnitude. Rapid injection of DNP hyperpolarized reagent into a high-resolution NMR spectrometer enables real-time NMR spectroscopy of the progressing reaction on a time scale of seconds. Model equations are described that allow the determination of reaction kinetics under concomitant influence of spin relaxation. Additionally, information on reaction mechanisms can be obtained by observing intermediate species or side products, whereby the transfer of atoms from a site on a reactant to a site on a reaction product can unambiguously be assigned. These techniques are applied to the study of metallocene catalysts in 1-hexene polymerization reactions. Two zirconium based catalysts giving rise to polymer with different tacticity are compared. In both cases, the time evolution of signals from monomer and polymer species is described by the combination of two kinetic processes for reaction and deactivation, respectively. Concomitantly, signals pertaining to a deactivation product are observed. In a second example, a ring opening metathesis polymerization catalyzed by a ruthenium catalyst is characterized. Here, the kinetic rates of formation of polymer units with specific stereochemistry can be determined separately in the growing polymer chain. Based on these results, real-time, D-DNP enhanced NMR spectroscopy is proposed as a method for the study of early events in polymerization reactions that does not require the use of synthetic isotope labeling strategies.