114g Discovery Informatics for Catalyst Design: Single Site Olefin Polymerization Catalysts

James M. Caruthers, W. Nicholas Delgass, Mahdi Abu-Omar, Kendall T. Thomson, Venkat Venkatasubramanian, Gary E. Blau, Thomas A. Manz, Grigori Medvedev, Jesmin Haq, Krista A. Novstrup, Khamphee Phomphrai, Shalini Sharma, and Balachandra B. Krishnamurthy

Single site polymerization catalysts are currently used industrially for the production of a variety of polyolefins with more precise molecular architecture than can be produced by more conventional polymerization methods. In single site polymerization there are a variety of kinetic processes, including catalyst activation and deactivation, chain propagation, chain transfer by beta-hydrogen elimination, etc. All of these reactions are mediated by the metal/ligand/counter-ion complex, where the key challenge is to first understand, and then rationally design, the ligands and the counter-ion to produce a polymer with a desired molecular architecture. The amount of data, both experimental and computational, that is needed to develop the necessary understanding is enormous.

We have employed a combined experimental, theoretical and informatics approach to determine the relationship between the catalyst structure and the rate of the various kinetic processes. We are studying Group 4 metal (i.e. Ti, Zr and Hf) catalysts that are ligated with a variety of aryloxides and Cp or Cp* with several different counter-ions. The catalysts are fully characterized by X-ray diffraction and NMR. The catalysts are used to polymerize a variety of α-olefins, including ethylene, propylene and 1-hexene, where the rate of polymerization in a batch reactor is followed by NMR. During the course of the polymerization, aliquots of the reaction mixture are removed and the evolution of the molecular weight distribution, and branching if present, is determined by GPC with refractive index, light scattering and viscosity detectors. A population balance model has been developed to describe the evolving molecular weight distribution, where the catalyst activation/deactivation rate constants, the propagation rate constant and the chain transfer rate constant(s) can be determined from the experimental data. Appropriate nonlinear statistical methods are employed to determine these rate constants and error associated with the rate constants. DFT quantum chemistry simulations have been used to determine molecular structure and the associated energies of a large number of catalyst/ligand/counter-ion/monomer systems, where we are currently developing relationships between descriptors of the molecular structure and the experimentally determined rate constants. We have developed a number of informatics tools to manage the large amounts of experimental and computational data as well as manage the significant computations needed to fit the kinetic models to the data. In addition, advanced visualization tools have been developed to enable the researcher to employ the human eye's high-bandwidth to process/interact with these large data sets. Using this combined experimental, computational and informatics approach, we have discovered catalysts that have significantly higher rates of polymerization.