

Olefin Polymerizations Using Cationic Ni(II) and Pd(II) Diimine Complexes

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A series of Pd(II) and Ni(II) complexes bearing bulky α -diimine ligands will be described which serve as catalysts for the polymerization of ethylene, α -olefins, and 1,2-disubstituted olefins. Microstructures of these polymers are unique. Branched polymers are produced from ethylene, and the extent of branching varies from “lightly” branched to hyperbranched depending on metal, ligand, ethylene pressure and temperature. Polymers generated from α -olefins and 1,2-disubstituted olefins exhibit chain straightening and fewer branches than expected based on sequential 1,2 insertions. This talk will focus on the description of polymer microstructures as well as detailed mechanistic aspects of the polymerizations. Low temperature spectroscopic studies employing well-defined initiators reveal catalyst resting states, barriers to alkene insertions, the nature of the cationic alkyl intermediates, and details of the chainwalking processes which are responsible for both branching in polyethylene and chain straightening in poly(α -olefins). The mechanistic details uncovered serve to explain the polymer microstructures observed and the substantial differences in behavior observed between the Ni(II) and Pd(II) systems.

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