Mechanistic insight into the neodymium-catalyzed polymerization of dienes and ε-caprolactone

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Neodymium based Ziegler-Natta systems are superior to the traditional Ziegler-Natta catalysts and other lanthanide-based Ziegler-Natta systems for the polymerization of dienes and lactones. The synthesis of the polymers from these simple monomers is complex due to the wide variety of materials obtained from tuning ligands, co-catalysts, temperature, solvent, and [co-catalyst]/[catalyst] ratios. Development of neodymium catalysts to obtain a living polymerization and control over molecular weight, polydispersity, tacticity, and microstructure are desirable. We recently demonstrated the neodymium phosphate-catalyzed polymerization of myrcene and ε-caprolactone (homopolymers and block copolymers). Herein, we provide a deeper understanding of the neodymium-catalyzed polymerization of myrcene and ε-caprolactone through experimental studies (crystal structure of the active complex, end-group analyses, reaction rates, kinetics, thermodynamics, reactivity ratios). These results may guide the logical design of new catalysts to give well-defined polymer properties and expand the scope of monomer substrates.