Jean RAYNAUD

Univ. Lyon, CPE Lyon, CNRS, Chimie Catalyse Polymères et Procédés (C2P2), UMR 5265, Villeurbanne

Understanding Iron Catalysis to design high-performance Polymers & Copolymers from $\alpha$-olefins & 1,3-diene

Harnessing sustainable catalysis has become a major workhorse of innovation in Chemistry. Iron is the most abundant transition metal in the Earth’s crust. Its high availability and low toxicity render it extremely attractive as a target for metal-based catalytic platforms. Interestingly for polymer chemists, well-defined molecular iron precatalysts provide the opportunity to also control selectivity through monomer selection/coordination/insertion when appropriately choosing the mode of activation. In our project, iron catalysis has proven particularly efficient in providing methods to both synthesize polyolefins from ethylene and $\alpha$-olefins and polydienes from 1,3-dienes.1-4 On the heterogeneous side, the combination of ferrous chloride on exfoliated MgCl2 with appropriate Lewis bases and acids provides an excellent Fe-Ziegler-Natta-type precatalyst, which once activated/alkylated displays activities on a par with Ti. On the homogeneous side, redox-active ligands such as iminopyridine- and bisimine-type bidentates confer unique reactivity to the iron centers, affording various oxidation states, as evidenced by Mössbauer and NMR spectroscopies.3-5 By adjusting sterics and electronics, excellent regioselectivity and stereoselectivity have been achieved in the production of polydiene-based elastomers.3,4 Very recently, the concept has been extended to the copolymerization of ethylene with 1,3-dienes.5 Using an advantageous catalyst switch and favorable Fe-Al transmetalations/chain-shuttling processes, and adjusting the ligand set, we were able to achieve random and/or block-copolymer structures from ethylene and other 1,3-dienes. Extensive NMR characterizations evidenced the novel structures. These copolymers display unique and valuable physical & mechanical properties, which was shown using DSC & rheology.5 The low cost, low toxicity, low catalyst loading, and high turnover frequency of the catalysts presented could translate, with appropriate development, into industrially relevant processes.
Keywords: Iron Catalysis, Ethylene, 1,3-Dienes, Stereoselective Polymerization, Ethylene/1,3-Diene Copolymerization

References
5. “Iron-catalyzed copolymerization of ethylene and 1,3-dienes to design statistical and block copolymers harnessing Fe-Al transmetalation reactions” A. A. R. Hmayed, M. Humbert, D. Gajan, S. Norsic, V. Monteil, J. Raynaud submitted manuscript