Beyond Metallocene Polymerization Catalysts - Opening Up the Periodic Table

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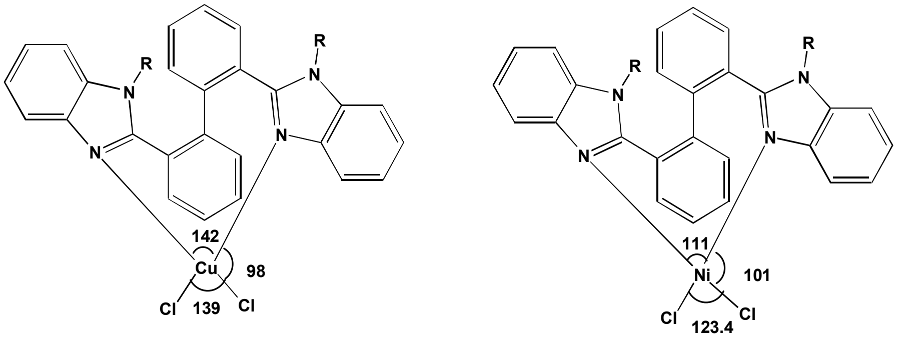
Polyolefins are by far the largest class of synthetic polymers made and used today. There are several reasons for this, such as being low cost, lightweight, and having high chemical resistance. Most of these polyolefins are manufactured using Ziegler-Natta catalysts, chromium-based catalysts or free-radical initiators.[1-4] The discovery of Group 4-metallocene catalysts for olefin polymerization has been one of the most important advantages in the last two decades. These catalysts not only improved the properties of the polyolefin porducts, but also made it possible to synthesize new types of polyolefins. Over the past few years catalyst development has moved from modifications of Group 4-metallocene catalysts to the search for yet newer catalysts, such as non-metallocene catalysts and late transition-metal catalysts. Some of the newer catalysts can produce novel polyolefin microstructures and functional polyolefins, which are not readily achieved with metallocene or Ziegler-Natta catalysts.

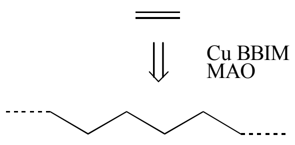
The synthesis of linear copolymers of olefins and polar monomers such as acrylates and vinyl acetate has been an elusive goal for polymerization chemists.[5] Polar monomers, such as acrylates or vinyl acetate tend to poison Ziegler-Natta and metallocene catalysts. Currently such olefin polar copolymers are produced by free radical polymerization procedures that tend to provide somewhat branchy copolymers.

Recently, there has been a flurry of activity in mid- and late-transition metal polymerizations.[6-10] The catalysts reported in the literature to this point are based on Group 8-10 metals (Fe, Co, Ni, Pd).[6-10] The lower oxophilicity and presumed greater polar-group tolerance of late transition metals, relative to early metals, make them attractive catalysts for the copolymerization of ethylene with polar comonomers, under mild polymerization conditions.

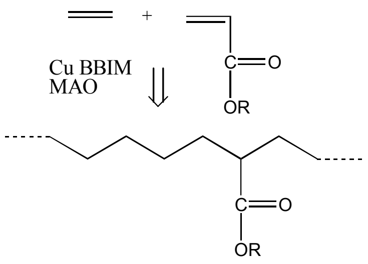


Cu(II) and Ni(II) Bis-Benzimidazole Complexes

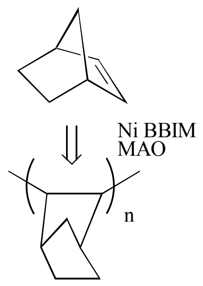
Olefin polymerization catalysts based on the more electron-rich Group 11 metals have also been recently prepared.[11-12] The Cu bis-benzimidazole pre-catalysts (activated by MAO) not only homopolymerize both ethylene and various acrylates but also copolymerize these two monomer classes. The ability of these catalysts to randomly copolymerize olefins with polar monomers via a metal-mediated mechanism is unprecedented. Nickel (II) bis-benzimidazole complexes on activation with MAO polymerize norbornene. The polynorbornene synthesized is a very high molecular weight vinyl addition product (*i e.* 2,3-linked); no ring-opened product is observed.[13] This talk will discuss the synthesis of novel Cu (II)- and Ni (II) - bis-benzimidaozle complexes and their use as olefin polymerization catalysts.



Highly Linear PE



In-Chain Copolymers



"Addition" Polymer

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