

Review

Recent developments in redox-active olefin polymerization catalysts

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ABSTRACT

Olefin polymerization catalysis is an ever-growing and ever-evolving field that is of strategic importance as scientists continually search for new methods to produce advanced polymeric materials. Polymerization catalysts are routinely used to regulate the incorporation of one or more monomers into a polymer chain, which can in-turn dictate the mechanical properties of the resultant material. If chemists are able to control when, how, and to what extent these monomers are polymerized, they can then selectively tailor materials to any targeted application. Significant efforts have been devoted to the development of advanced catalysts whose reactivity may be modulated *in situ* to produce a range of polymers varying in both their thermal and mechanical properties. To achieve the goal of catalyst modulation *in situ*, many scientists have turned to redox-active catalysis as a next-generation tool. This review discusses the recent evolution of redox-active olefin polymerization catalysts, which has extensively focused on the use of palladium and nickel-based catalysts. Furthermore, their ability to modulate catalytic activity, polymer microstructure, and even polyolefin grade will be described.

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1. Introduction

Polyolefins are a class of polymers derived from simple, inexpensive, and readily abundant olefinic monomer sources, such as ethylene, propylene, and higher α -olefins. Today, polyolefins represent a significant percentage of all polymers produced annually and can be tailored to exhibit a wide variety of thermal and

mechanical properties suitable for a plethora of applications. Polyolefins are most commonly synthesized using transition metal-based catalysts that enable polymerization via a coordination-insertion mechanism. The development of advanced olefin polymerization catalysts remains a heavily investigated area of research in both academia and industry alike, and leverages the complex relationship between ligand structure, the transition metal utilized, and overall reactivity to alter their polymerization behavior. It is through these studies that scientists have gained a deep fundamental understanding of how catalysts may be

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manipulated to promote polymerization control and thereby facilitate the synthesis of polyolefins with precisely defined structure at the monomeric and polymeric levels. Through these efforts, olefin polymerization catalysis is an ever-growing and evolving field that continues to push the forefront of synthetic polymer chemistry.

Historically, olefin polymerization was first independently discovered by the teams of Hogan and Banks, and Ziegler and Natta in the early 1950s [1–4]. Their pioneering work demonstrated that heterogeneous catalysts composed of Cr, Ti, and V could produce high molecular weight polyolefins, such as high-density polyethylene and isotactic polypropylene, which would radically change many of the materials we encounter each and every day [5]. While these catalysts have proven exceptional for producing high molecular weight polymers with broad molecular weight dispersity, their heterogeneous nature presents a complex catalytic environment in which multiple distinct active sites are present, each with its own distinct rate constants for propagation, chain-transfer, and termination events. This has encumbered detailed mechanistic and kinetic studies, and serves as a driving force to develop homogeneous, single-site catalyst analogues that may easily be studied, and thus controlled.

Homogeneous catalysts did not emerge as viable alternatives for olefin polymerization until the discovery of methylaluminoxane (MAO) by Kaminsky and coworkers [6–9]. MAO proved to be a crucial reagent for the efficient activation of homogeneous catalysts, and stimulated a paradigm-shift in how researchers studied, designed, and perceived catalysts for the coordination-insertion polymerization of olefins. Early examples of homogeneous catalysts focused heavily on group 4 metallocenes, which were highly active and single-site in nature, often displaying uniform chain propagation rate constants and producing polyolefins with narrower molecular weight dispersity than previously achievable using heterogeneous catalysts [10]. Following the success of metallocene-based catalysts, researchers soon expanded their scope of olefin polymerization catalysts to include ligands without cyclopentadienyl moieties [11]. These so-called post-metallocenes greatly expanded the breadth of applicable ligands and further promoted fine-tuning of ligand sterics and electronics surrounding the active transition metal center.

In 1995, the field of homogeneous single-site olefin polymerization catalysts was once again reinvigorated when Brookhart and coworkers demonstrated that late transition metal catalysts could also be employed to produce high molecular weight polyolefins [12,13]. These Ni and Pd α -diimine catalysts were shown to generate branched polyethylene microstructures using ethylene as a sole feedstock, which is a feat not currently possible with homogeneous group 4 catalysts [14,15]. Further investigations confirmed that these group 10 catalysts produce branched polymeric structures due to their strong propensity to migrate along the growing polymer chain via a process known as “chain-walking” [14]. Chain-walking is accomplished through β -hydride elimination and subsequent reinsertion of the pendant olefin, which if repeated, allows the active catalyst to shuttle along the polymeric backbone. If during that process a molecule of ethylene coordinates and inserts, a branching point is created. In addition to chain-walking, other attractive features of these group 10 catalysts include their ability to incorporate polar comonomers due to their decreased oxophilicity relative to their group 4 catalyst analogues, and also their ability to polymerize various olefins in a controlled/living manner [16–19].

Enticed by the many attractive features of Ni and Pd-based olefin polymerization catalysts, researchers soon directed their attention toward the development of innovative ways to modulate this unique catalytic behavior and improve overall polymerization control. One such example was described in 2005 by Guan and coworkers who synthesized a series of group 10 α -diimine

catalysts bearing various electron-withdrawing or electron-donating substituents [20]. Through this study, they discovered that catalysts bearing electron-donating groups produced more linear polyethylene microstructures, whereas those bearing electron-withdrawing moieties produce more highly branched materials. The authors concluded that the addition or removal of electron density at the active metal center alters the relative rates of monomer coordination-insertion to that of chain-walking. Although this report highlighted the pivotal role that ligand electronics play in regards to polymerization control, the need to iteratively synthesize multiple individual ligand/catalyst combinations with varying electron density ultimately limits this approach. Researchers soon turned to the possibility of utilizing redox-active ligands to bring about this electronic modulation using a single catalyst. Redox-active ligands provide a unique opportunity to modulate the electronic properties of an active metal center via the addition or removal of electrons from a single ligand framework (Fig. 1).

The first example of redox-switchable catalysis was reported by Wrighton and coworkers who demonstrated this concept via a diphosphino-cobaltocene ligated rhodium(I) complex in which the reduced form was found to hydrogenate cyclohexene approximately 16 times faster than its oxidized analogue (Fig. 2). This dramatic rate enhancement was attributed to increased electron density at the rhodium center that facilitates oxidative addition of H₂ [21]. This seminal work has since inspired the use of redox-active transition-metal catalysts for a plethora of small molecule transformations [22–25]. However, it wasn't until 2006 that this concept of redox-active catalysis would be applied to polymerization chemistry when Gibson, Long, and coworkers reported the first successful redox-switchable catalyst for the ring opening polymerization of lactide (Fig. 2) [26,27]. In this study, polymerization activity was turned “on” and “off” by adding or removing electrons from the ligands pendant ferrocenyl moieties, thereby altering its ability to coordinate and insert subsequent lactide monomers.

Inspired by the works highlighted above, analogous redox-active olefin polymerization catalysts were highly sought after and hypothesized to potentially provide a multitude of advantages stemming from the ability to precisely control catalytic activity and reactivity. Though the first successful examples of redox-switchable, or redox-active, olefin polymerization catalysts have only recently emerged, [28,29] it should be noted that the idea of

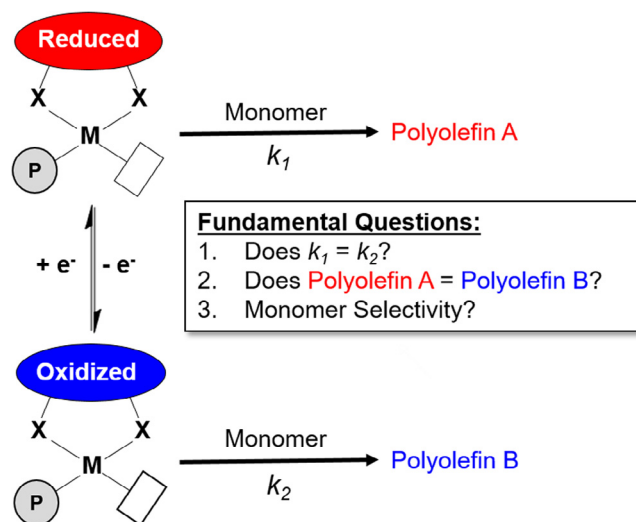


Fig. 1. Demonstrates potential of redox-active catalysis for olefin polymerizations.

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