Advanced Molecular Polyolefin Catalysis: Enabling Growth and Sustainability

Philip P. Fontaine, The Dow Chemical Company, Lake Jackson, TX

Abstract

The advent of molecular catalysis has fueled the development of new polyolefin materials with improved properties. In particular, the use of molecular catalysts affords an exquisite level of synthetic control, facilitating the tailoring of polyolefin microstructures. This, in turn, imparts new flexibility into the product design space, allowing for the production of materials with superior performance characteristics. With each year, new catalytic advances are made, further expanding the boundaries of the design space, and enabling the economical synthesis of novel polyolefins at the industrial scale.

Our research makes use of state-of-the-art high throughput instrumentation, and high level computational modeling, to arrive at unique combinations of catalytic properties. Sustainability is a key market driver for several of our recent commercial innovations, which include: resins with superior stiffness/toughness balance for light-weighting applications, and new olefin block copolymers (OBCs) for improved compatibilization and recycling.

Introduction

Linear low density polyethylene (LLDPE) comprises ca. 30% of the global polyethylene production, and increasing demand has led to continued growth in this market segment. This, in turn, has fostered an active area of research, as new polymer compositions with improved performance are sought.

LLDPE is produced via a copolymerization of ethylene and an alpha olefin; a coordination catalyst is used to enable the reaction, and the characteristics of the catalyst ultimately dictate the polymer microstructure (Figure 1).

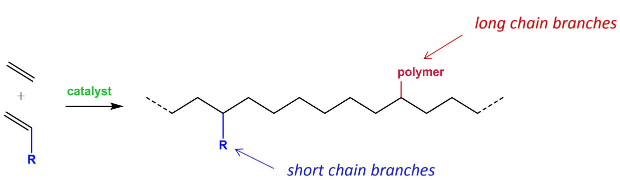

Figure 1. Production and characteristics of LLDPE.

Molecular polyolefin catalysts are often desirable for LLDPE production, by virtue of several favorable features which enable improved control of polymer microstructures, thus facilitating superior product designs. Desirable features include:

- Single site behavior
- Large range of ethylene / α-olefin selectivity
- Wide range of molecular weight building capacity
- Tunable branching distributions
- Capacity to engage in chain shuttling reactions

The above-mentioned features, in turn, translate into more flexibility with respect to product design. Therefore, molecular catalysis enables the production of fundamentally new polymeric materials.[1,2]

Advanced Molecular Catalysis

Our research is driven by three central capabilities: 1) high throughput instrumentation, 2) synthetic expertise, and 3) theoretical and mathematical modeling. These form the core of our discovery engine, which has fueled the progression of advanced molecular catalysis. Relative to the earlier generations (e.g. metallocenes and constrained-geometry catalysts, or CGCs), the newer generations (e.g. imino/amido and bis-phenylphenoxy) afford many differentiated and advantaged characteristics (**Figure 2**).[2] In this capacity, the evolution of new molecular catalysts through the years has, in turn, enabled advancements in polyolefin performance and/or facilitated more sustainable production processes. Ultimately, this has been critical for commercial success in the growing polyolefin markets.

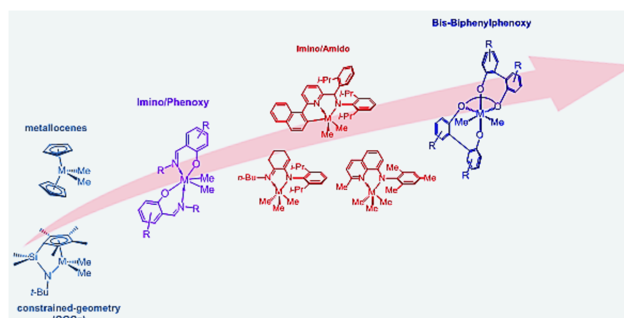

Figure 2. Evolution of molecular catalyst families.

One key advantage of molecular catalysis, relative to conventional Ziegler-Natta catalysis, is the capacity to produce discrete architectures. The result is a break from the traditional composition paradigm – a continuum from comonomer rich-low molecular weight chains to highly crystalline-high molecular weight chains – and the capacity to decouple and, independently, tune the two parameters. Therefore, new compositions are accessible, and designs can be finely tailored and modified to suit a variety of different end-use applications (**Figure 3**).

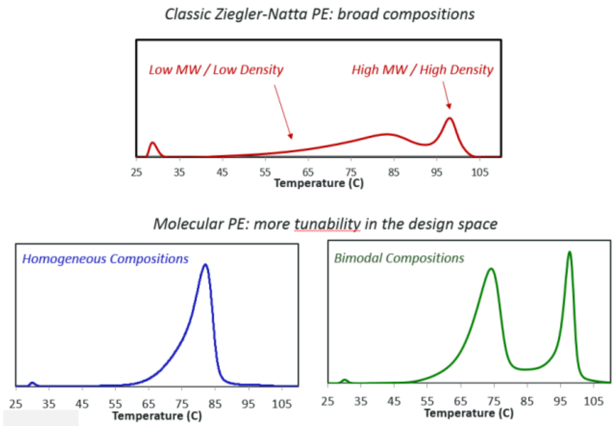

Figure 3. Comparison of compositions resulting from Ziegler-Natta and molecular catalysis.

Similarly, the capacity to produce long-chain branching is a hallmark of molecular catalysis, opening up yet another tuning parameter, and one with a critical impact on the resulting polymer properties. Architectures ranging from highly linear, to high branched, and everything in between, are available via molecular catalysis (**Figure 4**).

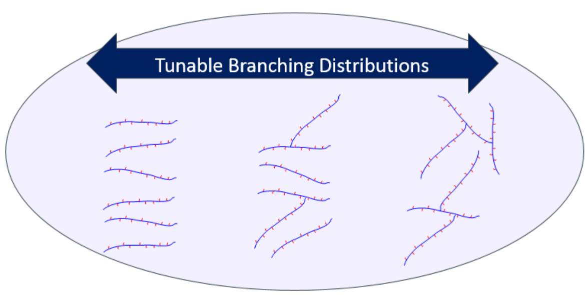

Figure 4. Tailored branching distributions enabled by molecular catalysis.

Finally, over a decade ago the unique capability of some molecular catalysts to engage in facile chain transfer reactions with other metal alkyls was harnessed to produce olefin-block copolymers OBCs – new to the world polymer microstructures.[1] Here again, molecular catalysis produced a new tool for materials scientists, resulting in designer polymers that broke the previously existing structure-property paradigms (**Figure 5**).

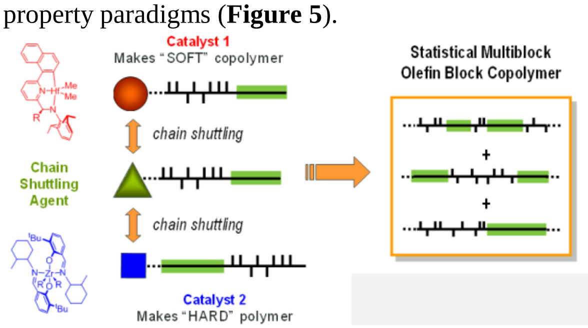

Figure 5. Chain shuttling catalysis and the production of olefin-block copolymers.

Commercial Successes

Recently, we have leveraged advanced molecular catalysis to produce the INNATE™ family of LLDPE, which exhibit superior stiffness-toughness balance. The unique balance of kinetic features imparted by the molecular catalyst unlocked a new design space, useful across several application spaces where exceptional mechanical properties are desired. INNATE™ resins enable down-gauging, an important stride toward reaching our sustainability goals. This innovative material was recognized with a Ringier award in 2016, and an R&D 100 award in 2017.

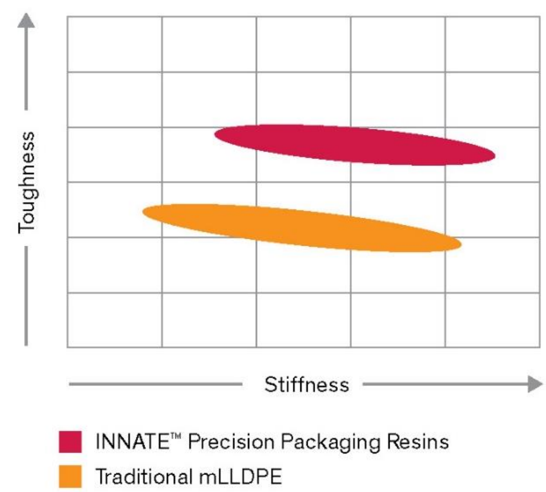

Figure 6. Improved stiffness-toughness balance with INNATE™ LLDPE.

Another recent realization of the new capabilities of advanced molecular catalysis is INTUNE™ OBC compatibilizers. These materials are particularly effective at compatibilizing polyolefin blends (e.g. PP with elastomers, LDPE, and HDPE), and multi-layered structures. The technology can be harnessed in many ways, such as improving performance characteristics (optics, adhesion, durability), or to provide a means to reduce complicated multi-layered structures into simpler ones. Moreover, INTUNE™ OBCs provide new opportunities for polyolefin recycling, which is again in line with our efforts to advance technologies that combine performance and sustainability.

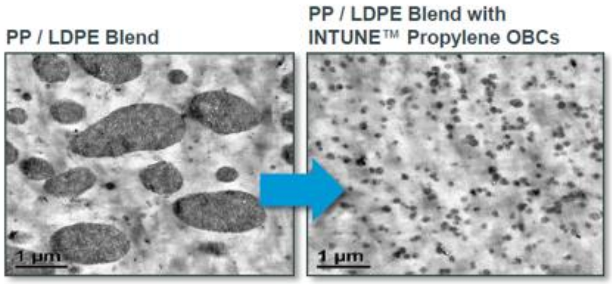

Figure 7. State of the art compatibilization with INTUNE™ OBCs.

Conclusions

The evolution of advanced molecular catalysis has resulted in catalyst systems with ever-improving performance, and, in turn, the commercialization of new polyolefin materials with advantaged performance continues to impact the growing market. Even after more than two decades of catalyst research, we are at the early stages of this trend, which will undoubtedly continue into the years ahead. At the same time, as the polyolefin markets continue to see growth and supplant legacy materials in a range of varying application spaces, the need to develop sustainable technologies is paramount. Therefore, the marriage of molecular catalysis with sustainable polyolefin solutions is a natural fit, and the challenges and opportunities are already being discovered.

™ Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow

References

1. Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714.
2. Klosin, J.; Fontaine, P.P.; Figueroa, R.; *Acc. Chem. Res.* **2015**, *48*, 2004.