Enabling a New Generation of Polyolefins

With a global production of 150 million metric tons in 2013, polyolefins represent the largest class of synthetic polymers. Their popularity stems from their versatility. Manufacturers can use different catalysts to stitch together small sets of inexpensive building blocks (olefins) and produce various grades of polyolefins for myriad markets and applications, from blown film to tennis racket strings.

The first polyolefins were created by Karl Ziegler and Giulio Natta, who won the Nobel Prize in Chemistry in 1963 for their achievement. Since then, industry has used a costly, time-consuming, "one catalyst, one material" trial-and-error approach to developing new polymers.

Precision Polyolefins (PPL), a spinout from the Univ. of Maryland (College Park), intends to change the status quo with a portfolio of proprietary and patented technologies. The company aims to establish a novel "one catalyst, many materials" paradigm for rapid discovery and product development of new polyolefins.

PPL seeks to develop new polyolefins for low-volume, high-value markets. The products could serve either as performance-enhancing additives for existing synthetic materials, formulations, or finished goods, or as replacements for materials that are at a disadvantage due to pricing, sustainability, or health and environmental concerns. Applications for PPL's products include adhesives, lubricants, and viscosity and surface modifiers.

PPL's breakthrough is based on a type of living polymerization, known as living coordinative chain transfer polymerization (LCCTP), invented by Lawrence Sita and colleagues at the university with funding provided by the National Science Foundation (NSF). LCCTP is a powerful technology that can convert ethylene (C2), propylene (C3), and longer-chain α-olefins into a diverse spectrum of precision polyolefins. The breakthrough method enables programmable control over chemical structure, chain length distribution (*i.e.,* polydispersity), and end-group functionality.

In a typical commercial polymerization process, an active catalyst inserts an olefin into a polymer chain — causing the chain to grow and increasing its molecular weight. In LCCTP, a second process occurs simultaneously with olefin insertion: rapid, reversible chain transfer.

LCCTP is conducted with a small amount of active transition metal catalyst, but unlike traditional polymerization, also a large stoichiometric excess of commodity zinc or aluminum alkyl. By itself, the excess metal alkyl cannot participate in olefin insertion. However, after the catalyst inserts an olefin into a polymer chain, it transfers the entire chain to the metal alkyl. The metal alkyl serves as a type of surrogate, or placeholder, site for the polymer chain, which allows shorter polymer chains to jump onto the catalyst so they can undergo olefin insertion and chain growth. The rapid, reversible polymer chain transfer occurs between active and surrogate sites at a rate that is substantially greater than the rate of olefin insertion — that is, the chains are jumping on and off the catalyst faster than they are growing. This helps to ensure that chain growth occurs at a steady rate across the species as a whole, thereby limiting polydispersity. The final polyolefin yield is greater than the yields that can be achieved by traditional living polymerizations due to the large excess of inexpensive metal alkyl that is employed.

At the end of the LCCTP process, every polyolefin chain has a reactive end group attached to it that can be treated with different reagents to produce a variety of polyolefin specialty chemicals with different functionalities. PPL produces its XPURE line of low- to ultralow-molecular-weight polyolefin oils in a range of grades with low polydispersity. Each grade has a specific molecular weight and unique physical properties (*e.g.,* viscosity and pour point). In contrast, polymers made by conventional processes have a very broad polydispersity, and the higher molecular weights in the batch control the physical properties.

LCCTP can also operate under conditions of stereomodulation, whereby the relative handedness of each C3 unit inserted into the growing chain is controlled as a function of time. This approach produces a new type of thermoplastic elastomer (TPE) with tunable elastic properties known as stereoblock polypropylene (sbPP).

"PPL's LCCTP technology can be a game changer for development of the next generation of advanced materials for many applications, including adhesives," says Edwin Hortelano, America's CTO for Bostik, Inc., one of the largest international adhesives companies. With funding provided by a Small Business Innovation Research grant from NSF, PPL overcame the major hurdles of moving LCCTP from the academic lab to successful validation within a 200-L commercial reactor that can now deliver 100-kg quantities of its XPURE oils and sbPP TPEs. The company has set its sights on 1-ton validation in 2015.

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