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MACROMOLECULES

# Polyolefin Shuffle

## Repeated chain transfer between two catalysts yields tailored block copolymers

Steve Ritter

Polymer chemists are always shopping around for new catalysts. A team of researchers at Dow Chemical found a bargain by identifying a pair of catalysts, with substantially different monomer selectivities, that permit formation of block copolymers by passing the growing polymer chains back and forth in a continuous process. This "chain-shuttling polymerization," which utilizes the common polymer-chain-transfer reagent diethylzinc, is expected to make tailored olefin block copolymers available on a commercially viable scale for the first time (*Science* **2006,** *312*, 714).


Dow Photo

**SHUTTLE CREW Dow chemists (from left) Arriola, Carnahan, Hustad, Kuhlman,**

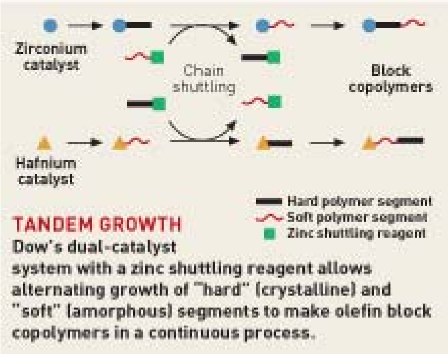
**and Wenzel developed chain-shuttling polymerization method.**

"This is a highly creative piece of science that goes well beyond normal olefin homopolymerization," comments chemistry professor Geoffrey W. Coates of Cornell University. "What's really exciting about the Dow work is that two catalysts identified by using a clever high-throughput screening technique were used to make block copolymers with high-melting polyethylene and low glass-transition temperature copolymer segments. This strategy opens a door to an entire new class of thermoplastic elastomers."

The Dow researchers include Daniel J. Arriola and Timothy T. Wenzel at the company's Midland, Mich., facility, and Edmund M. Carnahan, Phillip D. Hustad, and Roger L. Kuhlman at the company's Freeport, Texas, site. Key to their work was finding a pair of catalysts with very different selectivities for ethylene and for longer chain a-olefins that were capable of polymer chain shuttling using diethylzinc in a single reactor.

They settled upon a zirconium bis(phenoxyimine) catalyst for ethylene polymerization and a hafnium pyridylamide catalyst for 1-octene polymerization. The catalysts have bulky ligand systems tha restrict access to the metal centers, similar to metallocene catalysts typically used for commercial production of olefin homopolymers and random copolymers.

Diethylzinc is used in olefin polymerizations to terminate chain growth by transferring the polymer chain from the catalyst metal to zinc in exchange for an ethyl group. Usually irreversible, this process has been shown to be reversible in some cases. The Dow researchers took advantage of this reversibility to use the zinc reagent as a "reservoir" to hold polymer chains as they are intermittently shuttled between the catalyst molecules to grow alternating blocks of the two polymers.




TANDEM GROWTH Dow's dual-catalyst system with a zinc shuttling reagent allows alternating growth of "hard" (crystalline) and "soft" (amorphous) segments to make olefin block copolymers in a continuous process.

Adapted from *Science*

The team tested the dual-catalyst system by synthesizing a series of ethylene-octene copolymers. These elastomers have a useful combination of "hard" crystalline polymer with low octene content and "soft" amorphous polymer with high octene content for high-temperature applications. The rate of chain transfer, and thus the "blockiness" of the product, can be controlled by the concentration of the monomers and diethylzinc.

The continuous process has many advantages, the researchers say. For example, it leads to a better quality polymer than random copolymers or two polymers that are physically blended, and it does so in a more efficient, economical, and potentially greener way than current commercial copolymer batch production processes do.

The new process is "absolutely amazing," notes James C. Stevens, a Freeport-based Dow research chemist and olefin catalyst expert. "To be able to make new kinds of block copolymers from olefins with high catalytic efficiency and in a continuous process is a real breakthrough. The science behind this technology is fascinating, and we're excited about being able to provide our customers with new products."

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