

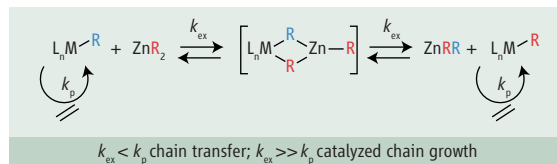
metal center to a dormant main-group metal species has been known since the early days of polyolefin catalysis. Its origin can be traced back to Karl Ziegler (7), who, in the early 1950s, discovered that a mixture of TiCl_4 and trialkylaluminums could catalyze the formation of polyethylene (hence founding metal-catalyzed polyolefin production). Ziegler postulated that the transition metal could be acting as a catalyst for the insertion of ethylene into the Al–C bond, a reaction which he termed a metal-catalyzed Aufbau reaction.

Ziegler soon realized that the titanium centers were responsible for catalyzing C–C bond formation, whereas the function of the Al species was to deliver an alkyl-initiating group to the transition metal. However, analyses of polyethylene samples generated by a variety of catalysts have revealed that aluminum alkyls readily engage in an exchange reaction with their transition-metal catalyst partners (6). Some have been found to do this very efficiently, to the extent that chain transfer to aluminum is actually faster than ethylene insertion into a metal-carbon bond. This regime, known as catalyzed chain growth (8) or degenerative group transfer (see the second figure), leads to chains with a remarkably narrow (< 1.1) and symmetrical distribution of chain lengths. The narrow molecular weight distributions can be used as an indicator of suitable chain-transfer behavior for the chain shuttling reaction.

Other main-group alkyls, including those of Mg (9), and more recently Zn (5, 10, 11), have also been shown to facilitate highly efficient chain transfer to and from transition-metal centers. Zn is among the most efficient chain-transfer reagents for single-site catalysts across the transition series, because the metal-carbon bond energies of the zinc alkyl closely match those of transition-metal alkyl species, the polarities of the Zn–C and M–C bonds are similar, and the mononuclear dicoordinated Zn centers are uncrowded.

To form microblock materials, two catalysts are used within a common pool of chain-transfer reagent (3); propagation must be faster than chain transfer to the main-group metal center, and the relative rates of chain transfer will dictate the average block lengths. Because the degree of chain transfer is affected by several factors—including the concentration of chain-transfer reagent, the concentration of monomer, and the temperature of the polymerization—it should be possible to find a set of conditions to allow the formation of the desired microblock structures.

However, the identification of catalysts that yield differentiated microstructures at appropriate rates of chain transfer presented a substantial challenge. By combining advances



Chain shuttling. Reversible alkyl-group exchange between dormant zinc and polymerization-active transition-metal centers can be used to tune the properties of the resulting polymers.

in single-site polymerization catalysis with powerful high-throughput screening methodologies, Arriola *et al.* have been able to home in on catalysts that enable both microstructural control and efficient chain shuttling. Moreover, they show that the catalysts can be used in a continuous process, which has the advantageous effect (from a polymer processing viewpoint) of broadening the molecular weight distribution; a broad molecular weight distribution allows the polymer to be extruded (pushed) through a narrow aperture. The shorter chains present in the broad distribution effectively lubricate the material.

Arriola *et al.* elegantly demonstrate the advantages of combining two catalysts and a single type of monomer with a shuttle reagent, but the plethora of materials that might prove accessible by using multiple catalysts and monomers can only be imagined at this point. Combining catalysts would add many additional and attractive possibilities. Because the polymer chains end up attached to a main-group species, the intrinsic reactiv-

ity of the main-group alkyl may potentially be harnessed to access end-functionalized products. For example, Zn alkyls react readily with gases such as oxygen to give Zn alkoxides, which can then be hydrolyzed to alcohols, or with CO_2 to form carboxylic acids; these may have applications as surfactants (for low-molecular-weight products) or as functionalized polyolefins with enhanced surface energies. This catalyst shuttle technology provides the long-sought platform for producing microblock polyolefin materials on a commercial scale.

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SOCIAL SCIENCE

The Pleasures and Pains of Information

George Loewenstein

Information serves not only as an input into decision-making, but is a source of pleasure and pain in its own right. This has diverse consequences for human decision-making.

In 1961, economist and Nobel Laureate George Stigler (1) initiated the “economics of information” when he relaxed an assumption that had dominated economics until that point. Rather than assume that people are fully knowledgeable of relevant information when it comes to making a decision, he allowed for the possibility that people might lack information and be motivated to acquire it. As Stigler noted when he accepted the 1982 Nobel Prize, “The proposal to study the eco-

nomics of information was promptly and widely accepted, and without even a respectable minimum of controversy. Within a decade and a half, the literature had become so extensive and the theorists working in the field so prominent, that the subject was given a separate classification in the *Index of Economic Articles*.” Stigler acknowledged that “The absence of controversy certainly was no tribute to the definitiveness of my exposition.” Rather, “All I had done was to open a door to a room that contained many fascinating and important problems” (2).

Relaxing the assumption of perfect information did, indeed, open new doors for econo-

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