Oscillating Catalysts: A New Twist for Plastics

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Polypropylene is relatively new in the plastics world, a 1950s product of the academic work of Ziegler and Natta (*1*) and the Phillips Petroleum industrial labs of Banks and Hogan (*2*). The raw material used in its synthesis is propylene, an oil-derived gas that is plentiful and therefore inexpensive, as is its polymer. Daily contact with polypropylene is inevitable: It is found in appliances, bottles, carpet, clothing, insulation, drinking glasses, everywhere. Yet as Coates and Waymouth report on page 217 of this issue (*3*), even material as mature as polypropylene can be the subject of dramatic advances in polymer chemistry.

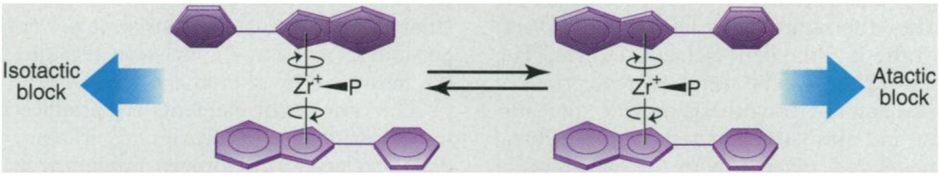
Ziegler and Natta won the 1963 Nobel Prize for their work in stereoregular polypropylene. Stereoregularity is the key to useful polypropylene because it leads to strength and ease of processing, and without this discovery, the polymer would be of little value. Instead, it is among the five largest volume plastics in the world, with billions of pounds being produced annually.

How did Ziegler and Natta generate stereoregular polypropylene? The chemistry begins with a fixed chiral (stereoregular) center found within the catalyst itself, and this center initiates a chain reaction of tens of thousands of molecules of propylene to produce the polymer. The reaction is extraordinarily fast, with each new propylene unit being inserted into the growing polymer one at a time. The amazing aspect of Ziegler-Natta chemistry is that each insertion of propylene occurs with nearly perfect stereochemical precision, thereby producing the same stereocenter each time.

Stereoregularity can be described in terms of the "tacticity" of the polymer that is formed. For example, if all the stereocenters in the polymer are the same, then it is said to be "isotactic." If the stereocenters alternate back and forth in their identity, then the polymer is "syndiotactic." If there is no control of stereochemical placement, then the polymer is "atactic." While isotactic polypropylene is by far the most important form of the material in use today, the syndiotactic polymer is now being made available, and even the atactic polymer is finding uses.

An enormous amount of work has been done in this field since the Ziegler-Natta discovery (*4*), and so one would expect that most all the mechanistic details associated with polypropylene catalysis would have been elucidated. Not so.

We are experiencing a renaissance in polypropylene catalysis based on a series of compounds known as metallocenes. Conceptually, these catalysts operate in a manner much the same as Ziegler-Natta catalysts, yet their molecular structure is more finely tuned to the polymerization work at hand. This metallocene research has led to a totally new concept in polypropylene catalysis, which is described in the report by Coates and Waymouth (*3*). They describe a way to turn plastic polypropylene into elastic polypropylene, thereby opening completely new markets for its use. The discovery is a clever one, and again, the magic is in the catalyst itself.



Spinning out polymer. The "top" and the "bottom" groups in the catalyst, called substituted indenyl groups, oscillate or spin about the zirconium metal center. In one position, they form stereoregular polymer. In other positions, nonregular polymer forms. This freedom to oscillate is the essence of the discovery that leads to elastic polypropylene.

Today's polypropylene is a plastic because only one type of stereoregularity (either the isotactic or the syndiotactic form) dominates the structure of the polymer. This order exists because the Ziegler-Natta catalysts possess a fixed stereochemical center. Decreasing the polymer's stereoregularity dominance by manipulation of Ziegler-Natta catalysts can give elastic polypropylene (in fact, Natta produced the first elastic sample of polypropylene), but how this happens is not well understood, hard to control, and has not led to large-scale use.

On the other hand, Coates and Waymouth describe a rational catalytic approach to reducing this dominance. Their catalyst oscillates between stereochemical forms, rather than remaining fixed like the Ziegler-Natta systems. The consequence is the production of a polymer chain that possesses running lengths of isotactic stereocenters connected to running lengths with no stereocontrol (atactic centers). The material is called a stereoblock polymer. Isotactic dominance is reduced, and elasticity emerges from the presence of the atactic form of the polymer.

The figure shows this oscillating catalyst in action and displays the essence of the concept. The substituted indene rings on the top and the bottom of the zirconium metal center are free to spin, and as they do, they lead to different stereochemical forms of the catalyst. Consequently, different stereochemical forms of the polymer are formed as the chemistry proceeds. Find a way to control the rate of spinning with respect to the rate of propylene placement in the growing polymer chain, and one can control elasticity very well.

This is what the authors have done. By placing substituents on the indene ring, they have controlled the rate of oscillation, thereby permitting running lengths of isotactic and atactic stereochemistry to occur. The amount of time spent by the catalyst in each rotational position determines the amount of a given stereochemistry that is generated. Increase the pressure (concentration) of propylene in the reactor, and the running lengths of isotacticity are increased. Thus, the properties of the elastic polymer can be controlled rather easily, and consequently the material can be made elastic, much like a rubber band, or simply tough, like the material found in shoe treads.

These are truly exciting results, stimulated by the efforts of Chien, Collins, and others active in this research area (*5*). The research will continue to define the types of substituents on oscillating rings that control the oscillation rate more effectively. Even so, today's Coates-Waymouth catalyst system lends itself to existing manufacturing facilities, and it should be possible to tailor polypropylene to specific applications.

References

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