production of ATP, membrane leakiness may lead to subtle changes in ATP availability, causing reduced activity of this enzyme at lower temperatures than would be required for the inhibition of other photosynthetic reactions. The increased thylakoid leakiness at or below 35°C is rapidly reversible and at moderate temperatures can be partly compensated for by increased cyclic photophosphorylation (which uses photosystem I to boost ATP synthesis) (*8*). Very high temperatures (45°C and above) may irreversibly damage the photosynthetic machinery by causing the disintegration of the protein complex responsible for oxygen production during photosynthesis (*9*).

The substantial effects found by Murakami and colleagues after they reduced the level of membrane lipid unsaturation may reflect the specific double bonds they eliminated. They silenced the *FAD7* gene, which encodes a chloroplast-localized ω-3 desaturase. This enzyme converts 16:2 fatty acids (16 carbons long with two double bonds) to 16:3 molecules, or 18:2 fatty acids to 18:3 molecules, by desaturating the third to last carbon-carbon bond (see the figure). Other studies have used chemical hydrogenation (*10*) (which randomly saturates double bonds) or mutation to bring about fatty acid desaturation at other depths within the membrane (*11*). Some plants with decreased lipid unsaturation exhibit variation in chloroplast structure (*12*)—this makes it more difficult to demonstrate specific effects on thermotolerance.

Murakami *et al.* showed that their transgenic plants grew much better than controls at higher temperatures. Differences in growth rate were noted at 36°C, and transgenic plants survived for 2 hours at 47°C, a treatment that killed their wild-type counterparts. This demonstrates that thermotolerance is related to membrane properties, and that the growth and survival of plants can be determined by the thermotolerance capabilities of photosynthesis. With increasing concentrations of greenhouse gases in the atmosphere, the effect of high temperature on plants is an important area of study. The Murakami *et al.* report may provide valuable information about the best approach to engineering plants that can carry out photosynthesis in the face of heat stress.

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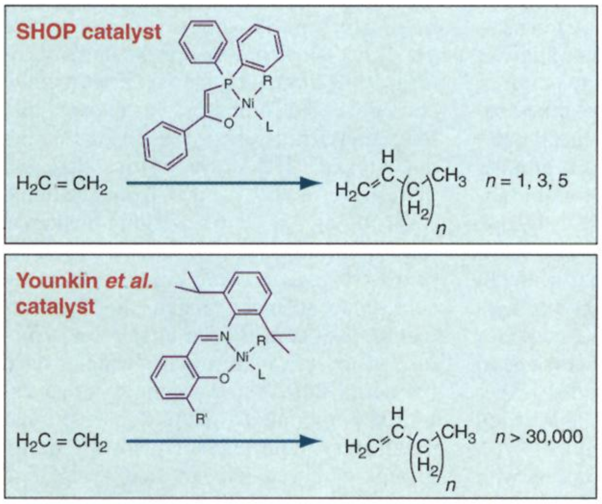
PERSPECTIVES: POLYMER CHEMISTRY

Nickel Comes Full Cycle

Eric N. Jacobsen and Rolf Breinbauer

Some of the greatest scientific discoveries have resulted from what at first seemed to be failed experiments; famous examples include Fleming's discovery of penicillin or Penzias's and Wilson's discovery of the cosmic background radiation. The modern era of polyolefin chemistry, which has helped to make plastics an important presence in our everyday lives, also has its origins in such an experiment. In 1953, Erhard Holzkamp, a doctoral student working under Karl Ziegler at the Max-Planck-Institute for Coal Research in Mülheim, Germany, was struggling to reproduce a reaction discovered in Ziegler's lab a few years earlier. In this so-called "Aufbau" reaction, a molecule of ethylene is inserted into the carbon-metal bonds of triethylaluminum. Careful investigation revealed that nickel impurities, which were introduced by cleaning the stainless steel reaction vessel with acid, were inhibiting the Aufbau reaction in Holzkamp's experiments, a phenomenon that came to be known as the "nickel effect" (*1*). The observation of such a drastic change in reactivity imparted by small amounts of a transition metal salt led the Ziegler lab to carry out a systematic study of the effect of salts of other elements on the Aufbau reaction. To their surprise, they observed that the addition of early transition metal halides, such as $TiCl_3$ or $ZrCl_4$, to trimethylaluminum led to a completely different type of catalyst—one that affected the polymerization of ethylene at room temperature and ambient pressure, resulting in the formation of a polymer with unprecedented properties. Giulio Natta soon discovered that these new catalysts also catalyzed the stereoregular polymerization of monosubstituted olefins (α-olefins). The importance of these discoveries is reflected only in part by the fact that Ziegler and Natta were awarded the Nobel Prize for chemistry less than a decade after Holzkamp's initial struggles. More than 40 million tons of polyolefins are produced by Ziegler-Natta polymerization every year, and these "plastics" impact our daily lives in countless beneficial ways.



Nickel catalysts. (Top) The SHOP catalysts oligomerize olefins. **(Bottom)** Younkin *et al.*'s new catalysts polymerize olefins. These catalysts are tolerant of polar functional groups and thus overcome one of the major limitations of Ziegler-Natta catalysts.

The initial discoveries made by Ziegler and Natta inspired an extraordinary level of research activity that has been sustained for the past three and a half decades. This can be ascribed to the fact that, although the Ziegler-Natta polymerization answered a crucial practical concern through the introduction of low-cost, high-quality polyethylene and polypropylene polymers, it left many questions unanswered. One of the most intriguing of these is whether it might be possible to polymerize olefins

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having polar functionality, which might result in polymers with new and exciting properties. On page 460, Younkin *et al.* report a major advance that may open the door to such new polymers in the near future (*2*). Their result represents the culmination of two lines of research that diverged from the initial work on Ziegler-Natta catalysts and are reunited in the present work.

One line of research aimed to understand how the Ziegler catalysts work. The nonuniformity of the active sites in these heterogeneous catalysts renders mechanistic study and rational design of modified catalysts extremely difficult. The search for soluble, single-site catalysts was finally rewarded when the groups of D. S. Breslow and Natta discovered that soluble metallocene complexes of early transition metals, when activated by dialkylaluminum halides, were capable of polymerizing ethylene. The introduction of methyl aluminoxane (MAO) as a cocatalyst by H. Sinn and W. Kaminsky boosted the initially low activity of these metallocene catalysts and allowed the polymerization of olefins other than ethylene. This raised the question of how to control the stereoselectivity in the polymerization of α-olefins, which is crucial for influencing the physical properties of the polymers. The development of chiral metallocene catalysts by Brintzinger laid the foundation for the creation of a catalyst "tool-box" that allows the construction of polyolefins with predictable properties, and some of these have just recently been introduced onto the market (*3*).

Despite the great progress made with these metallocene catalysts, one fundamental limitation remains: The highly electrophilic nature of the metal in these early transition metal catalysts generally makes it impossible to use olefins with polar functional groups as monomers or comonomers. Accordingly, a second line of investigation that grew out of the Ziegler and Natta work was aimed toward developing late-transition metal catalysts that might prove more tolerant of polar functionality. Ironically, the first major advances in this area arose from investigation of the "nickel effect" described above. Seminal work by Keim revealed that a nickel complex bearing a ligand that chelates through phosphorus and oxygen atoms (see the figure) catalytically converts ethylene to linear oligomers with chain lengths of between 4 and 20 carbon atoms. This reaction is the foundation of the Shell Higher Olefin Process (SHOP), a commercial process with many applications including the manufacture of detergents (*4*). The SHOP catalyst exhibits high tolerance of polar functional groups such as alcohols or esters, a result of the less oxophilic nature of nickel.

What remained to be done was to combine the best features of the metallocene catalysts with those of the nickel chelate catalysts, and functional group-tolerant polymerization catalysts should result. This, of course, is much more easily said than done, but in effect this is precisely what Younkin *et al.* have accomplished. Through a careful mechanistic analysis of the SHOP systems, they devised a new nickel-based catalyst that incorporates an NO chelate ligand and allows the polymerization of ethylene at ambient temperature and moderate pressure, even without the addition of a cocatalyst (see the figure). The resulting polyethylene is of high molecular weight and exhibits a low degree of branching in the polymer chain. This stands in sharp contrast to the highly branched polymers formed by other known late transition metal cationic catalyst systems (*5*). Most important, perhaps, is the unprecedented functional group tolerance of the new catalytic systems. Polymerizations can be carried out in the presence of polar impurities—severe poisons for Ziegler catalysts—and functionalized olefins can be used as feedstocks.

The discovery of highly active, neutral, single-site late transition metal polymerization catalysts raises several important questions. What sorts of polymers bearing polar functional group can be made and what will be their properties? Will hydrophilic or biodegradable polymers be readily accessible? How can the new catalysts be modified to allow stereoregular polymerization of functionalized α-olefins? One thing is clear, however: The present results will provide the basis for a huge amount of future research, and nickel will be at the middle of it all. This seems only fitting for the metal that inspired the modern era of polyolefin chemistry by serving as the source of Holzkamp's frustrations.

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PERSPECTIVES: TRANSCRIPTION

A Tail of Histone Acetylation and DNA Recombination

Mark S. Schlissel

In the 1960s, molecular biologists first noticed that addition of acetyl groups (acetylation) to histone proteins (constituents of nucleosomes around which the DNA is wrapped) is associated with transcriptionally active regions of the genome (*1*). More recently, many proteins that regulate transcription have been observed to possess (or recruit) histone acetyltransferase (HAT) or histone deacetylase (HDAC) activities that add or remove acetyl groups from proteins, respectively (*2*). The emerging notion is that a sequence-specific DNA binding protein brings histone acetyltransferase activity to an inactive gene in the chromatin. This results in a change in structure of the chromatin and an increase in the accessibility of the gene to other essential components of the transcriptional machinery. The transcription of many groups of genes is regulated by histone acetylation. A report by McMurry and Krangel on page 495 of this issue (*3*) now adds V(D)J recombination in T and B lymphocytes to the list of those reactions potentially regulated by histone acetylation.

Antigen receptors, such as immunoglobulin (Ig) in B cells and the T cell receptor (TCR) in T cells, are encoded by a series of V, D, and J gene segments that are spliced together in different combinations to provide a large repertoire of antigen receptors with different specificities. The assembly of these gene segments into functional Ig and TCR genes during lymphocyte development depends on a site-specific DNA recombination reaction termed V(D)J recombination (*4*). This combinatorial mechanism allows the genome to encode an enormous diversity of antigen receptor molecules with a relatively modest investment of genetic material. All rearranging gene segments are flanked by highly conserved recombination signal sequences. A protein complex containing the lymphoid-specific recombinase

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