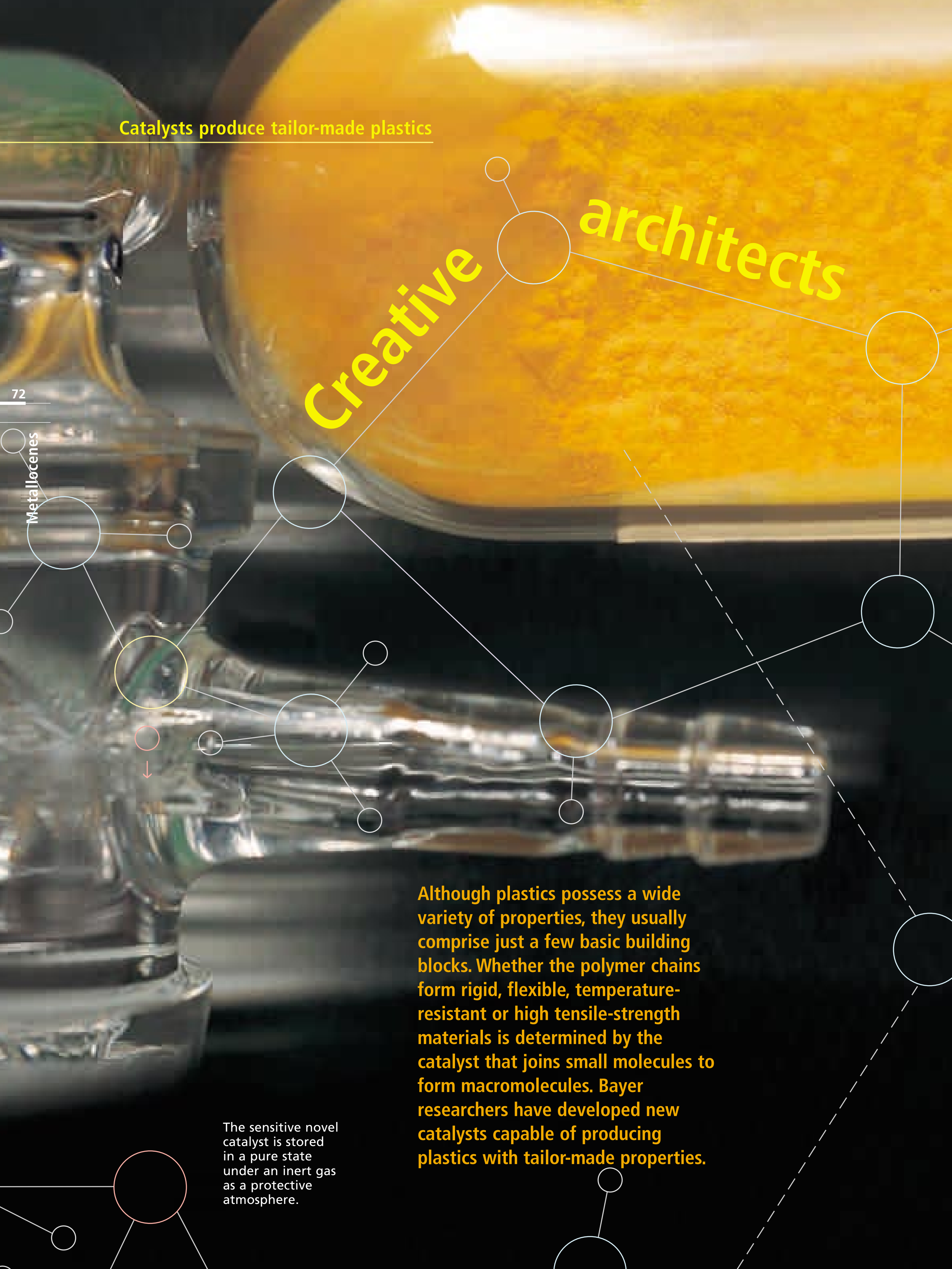
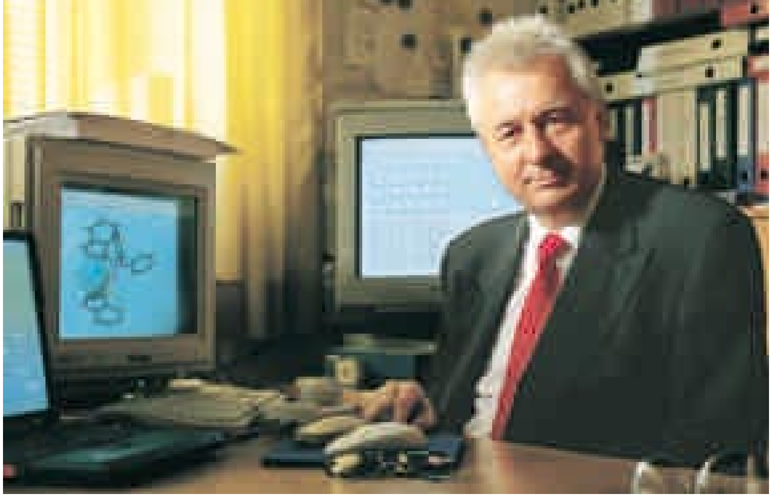


Creative architects

Although plastics possess a wide variety of properties, they usually comprise just a few basic building blocks. Whether the polymer chains form rigid, flexible, temperature-resistant or high tensile-strength materials is determined by the catalyst that joins small molecules to form macromolecules. Bayer researchers have developed new catalysts capable of producing plastics with tailor-made properties.

The sensitive novel catalyst is stored in a pure state under an inert gas as a protective atmosphere.



Dr. Aleksander Ostoja Starzewski developed the innovative D/A metallocenes, which he uses to create custom-made plastics.

D/A metallocenes

In a way, manufacturing plastics is like playing with a huge pile of Lego blocks. Even though the little pieces are all identical, they can be combined to build completely different structures. There are no limits to a child's imagination; he can create an endless number of new objects from the exact same building blocks.

The nature of the game is very similar for chemists making polymers, the materials we commonly refer to as plastics: they repeatedly recombine the same building blocks to conjure up materials that have a different appearance and new properties every time.

The most important tools polymer experts have at their disposal are catalysts, or molecular pacemakers that control and accelerate chemical reactions without themselves being consumed in the process. In the production of polymers, catalysts are responsible for joining identical starting molecules into larger structures known as macromolecules. The shape of these polymer structures, the length of the macromolecules, how they are entangled and crosslinked by lateral branches and nodes – all of these properties are determined by the catalyst.

Chemist Dr. Aleksander Ostoja Starzewski is one of the creative catalyst engineers and project managers working in the Innovation department of Bayer Polymers on the continuous development of new and improved "linking machines" for designer polymers. He specializes in catalysts for the production of polyolefins, including the well-known plastics polyethylene and polypropylene. Comprised of just a few carbon and hydrogen atoms, the basic building blocks of these plastics are tiny ethylene and propylene molecules chemists refer to as "olefins". Depending on how the catalyst joins these molecules, the resulting plastics can be thin and crinkly like fruit-and-vegetable bags at the supermarket, or rigid like the jewel cases of compact discs.

Making plastics with specific properties

A few years ago, Ostoja Starzewski made significant progress by developing a group of versatile catalysts known as "D/A metallocenes". These high-performance catalysts combine the best properties of the various metallocenes, making it possible to control polymer synthesis processes even more precisely and thus significantly improve the quality of the resulting plastics.

The production of plastics in the polyolefin range was a matter of trial and error for many years. Before a plastic with the desired properties was obtained, researchers repeatedly had to vary experimental conditions and see if they obtained the product they were hoping for. Making progress was an arduous task. The first breakthrough came in the mid-1950s with development of the Ziegler-Natta catalysts. These catalysts are mixtures of chemical compounds – of unknown molecular structure in some cases – to which the olefins bond to form macromolecules of various lengths. The problem was that Ziegler-Natta catalysts have several active sites where polymerization takes place simultaneously. The result is similar to that of a bunch of kids playing with a big pile of Lego blocks: a diverse mixture of polymer

Small amount – big effect

Working at the Max Planck Institute for Carbon Research in Mülheim an der Ruhr, Germany, chemist Karl Ziegler discovered in 1953 that, contrary to established practice, small ethylene building blocks can be joined to form long polyethylene chains even at room temperature and without application of external pressure. The key to his discovery was a special catalyst made of titanium tetrachloride and alkyl derivatives of aluminum. In recognition of this development, Ziegler and his partner Giulio Natta were awarded the Nobel Prize for Chemistry in 1963. In 1985, Hans H. Brintzinger, a researcher in Lake Constance, and his colleague Walter Kaminsky in Hamburg demonstrated that metallocenes are eminently suited as catalysts for stereospecific polypropylene synthesis. Metallocenes are highly superior to Ziegler-Natta catalysts. For example, 100,000 kilograms of plastic can be synthesized with just 100 grams of a metallocene.

The D/A metallocenes developed by Bayer combine and by far exceed the performance capacities of the individual metallocenes.

Werner Amann inspects the integrity of the high vacuum apparatus (right) required to manufacture the highly sensitive catalysts.

molecule chains with different lengths and branching patterns; no chance of obtaining specified properties.

Then, in the early 1980s, a new age began with another class of catalysts that had long been ignored: the metallocenes. These catalysts have only one active site where the starting molecules are linked. Consequently, they produce largely identical molecular chains in orderly fashion. It became considerably easier to optimize the old polyolefins and develop new ones. The polymer world was soon abuzz with news of the “metallocene revolution”.

Metallocenes resemble a molecular “mouth”, with two rings of molecules forming the upper and lower jaws and in between an olefin-devouring metal atom: the active site at which individual olefins are linked to form polymers. Most importantly, the first metallocene catalysts were capable of combining small ethylene molecules into linear polyethylene chains of comparable length. That improved the quality of polyethylene – films and plastic bags became more tear-resistant.

Later on, the upper and lower jaws of the metallocenes were hinged at the back, or “bridged” as chemists say. As a result, the “mouth” opened wide towards the front at a predefined angle. The active metal site was more accessible, allowing the joining of even relatively large olefins.

“Bridged metallocenes made it possible to produce strictly isotactic polyolefins,” says Bayer chemist Ostoja Starzewski. Isotactic polyolefins are long, absolutely uniform chains of carbon atoms. Lateral branches all pointing in the same direction are located on every other atom. This arrangement is the critical feature: thanks to the perfect microstructure, the uniform molecules crystallize to form a high-melting polymer. Isotactic polypropylenes can be used to manufacture tubes, camping cookware or plastic housings that are harder and stiffer than anything ever before produced with polypropylenes. However, because the metallocene catalyst with its defined structure was only suitable for forming very specific polymers, every new polymer molecule structure had to be laboriously developed on the basis of a new catalyst.

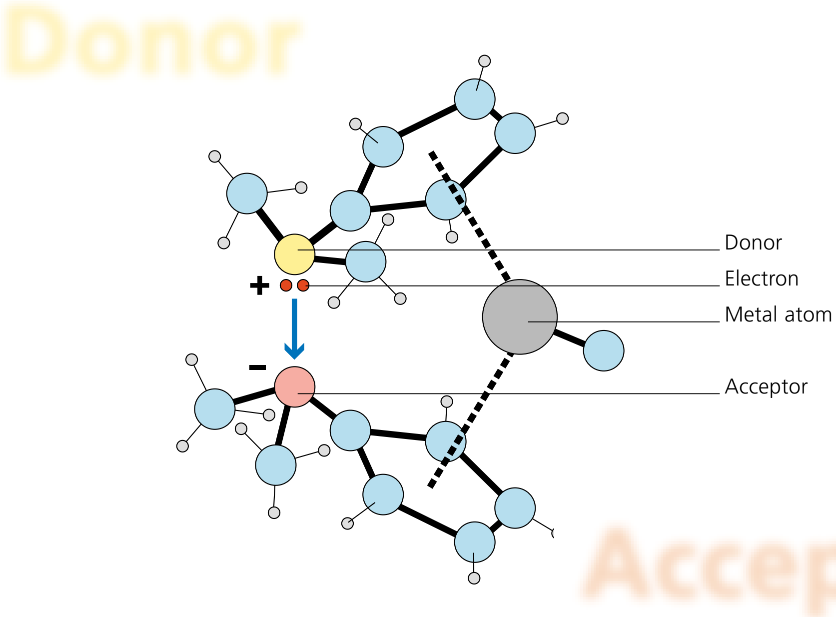
Worldwide consumption of plastics

214 million tons of synthetic polymers were consumed worldwide in 2001, according to an article in the German publication Nachrichten aus der Chemie, Vol. 3/2003.The total is divided among different types of plastic:

Plastic	Example application	Percentage
Polyethylene (PE)	Bags	24 %
Polypropylene (PP)	Pipes	14 %
Polyethylene terephthalate (PET)	Beverage bottles	14 %
Polyvinyl chloride (PVC)	Floor coverings	12 %
Polystyrene (PS)	Disposable food packaging	6 %
Engineering plastics (incl. blends)	Automotive manufacturing	7 %
Synthetic elastomers	Tires	4 %
Polyurethane (PU)	Mattresses	4 %
Other		15 %

Metallocene catalyst: A microscopic molecular mouth

“What we needed was a group of catalysts that united the best properties of all the different metallocenes,” explains Ostoja Starzewski. His idea was to create a metallocene with a “mouth” that could be widened or narrowed. In other words, a flexible olefin linking agent capable of building large or small, branched or unbranched precision macromolecules to specification.

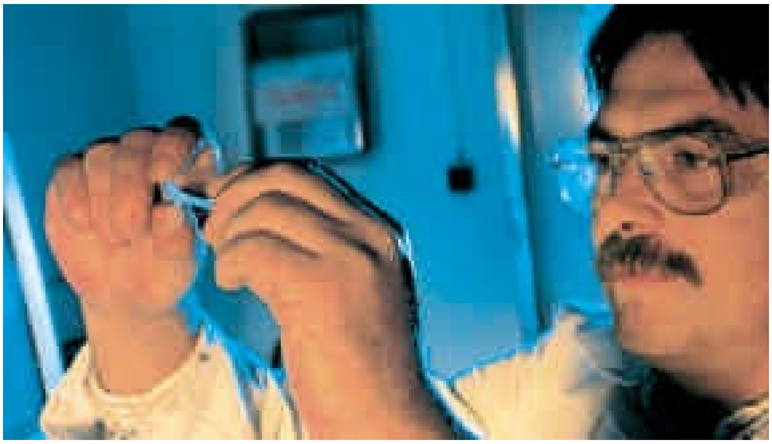


Controlled access for molecules
D/A metallocenes resemble a molecular “mouth”, with two rings of molecules forming the upper and lower jaws and in between an olefin-devouring metal atom. Electrons are transferred from one molecular jaw to the other. The electron flow subjects the two molecular components to an attractive force that bends the metallocene. If the attractive force between the electron donor and the electron acceptor is low, the mouth opens only slightly and allows primarily small molecules to pass through. If the attractive force is high, the mouth gapes open, additionally allowing large molecules access to the active metal site.

Ostoja Starzewski and his staff knuckled down to the task and soon discovered how the idea could be realized: the researchers modified the metallocene bridge in such a way that they could control the opening and closing of the molecular mouth. This they achieved by incorporating what are known as “Lewis bases” and “Lewis acids” in the metallocene molecule. The effect was to shift electrons and produce molecular components of opposite charge, which attract one another at different intensities, depending on the charge, thus bending the metallocene. Because this process can be undone by the molecule, the “mouth” can open and close periodically. Chemists referred to these components as “electron donors” and “electron acceptors”, thus giving birth to the name “D/A metallocenes”.

After defining and implementing the basic idea, the next step involved painstaking detail work. First, the Bayer chemists had to find out which molecular ingredients they needed to make the optimum D/A metallocene and which donors and acceptors provided the desired properties in the finished polymers. “Of course, the temperature at which polymerization takes place also alters the activity and function of a catalyst,” says Ostoja Starzewski.

Today, olefin polymers can be given virtually any combination of properties. Polypropylene is an illustrative example. Explains Ostoja Starzewski: “Depending on the catalyst selected, we can turn the simple and inexpensive building block propylene into extremely rigid polymers with ultra-long macromolecules and long lateral branches, or soft elastomers that make things like plastic car bumpers tough and therefore impact-resistant.”



Joachim Peckhaus checks the tensile strength of a plastic part prior to testing.

Starzewski hopes these materials will one day replace mass-produced PVC plastics, which are versatile but problematic when burned.

Ostoja Starzewski has since applied for more than ten patents all over the world. Bayer intends to exploit flexible D/A catalysts in the near future, although some of these molecular wizards will also be licensed to other companies.

We have only just begun to comprehend the full potential of D/A metallocenes. After all, even the first metallocene revolution had a far-reaching effect on practical applications. Polyethylenes exist today that are bulletproof and simultaneously more durable than conventional carbon fibers for making protective vests. Another advantage of these innovative catalysts is their compatibility with existing processes in plastics production, although the cost-efficiency of processing is still a factor requiring improvement. Powered by the adaptability of polyolefins, an enormous market has emerged in just a few decades: over 80 million tons are produced around the world each year, making polyolefins by far the largest selling chemical products. As it looks now, D/A metallocene catalysts are making the future of these plastics even more promising.

http://www.psrc.usm.edu/macrog/mcene.htm
Visit the University of Southern Mississippi web site for more information on metallocenes.