A **Ziegler–Natta catalyst**, named after [Karl Ziegler](http://www.facebook.com/pages/w/107921949230129) and [Giulio Natta](http://www.facebook.com/pages/w/111978655486302), is a [catalyst](http://www.facebook.com/pages/w/107820472585705) used in the synthesis of [polymers](http://www.facebook.com/pages/w/110191109010354) of 1-alkenes (α-olefins). Two broad classes of Ziegler–Natta catalysts are employed, distinguished by their solubility:

* Heterogeneous [supported catalysts](http://www.facebook.com/pages/w/162403960497179) based on titanium compounds are used in polymerization reactions in combination with cocatalysts, [organoaluminum](http://www.facebook.com/pages/w/112323632116140) compounds such as [triethylaluminium](http://www.facebook.com/pages/w/104484872981525), Al(C2H5)3. This class of catalyst dominates the industry.
* Homogeneous catalysts usually based on complexes of Ti, Zr or Hf. They are usually used in combination with a different organoaluminum cocatalyst, [methylaluminoxane](http://www.facebook.com/pages/w/132963376742243) (or methylalumoxane, MAO). These catalysts traditionally include [metallocene](http://www.facebook.com/pages/w/138270972858479)s but also feature multidentate oxygen- and nitrogen-based ligands.

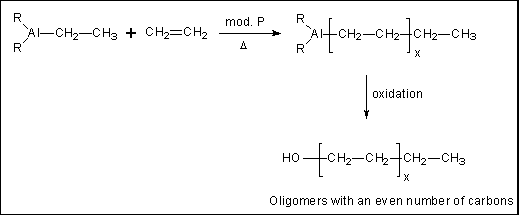
Ziegler–Natta catalysts are used to polymerize terminal 1-[alkene](http://www.facebook.com/pages/w/103131653060586)s (ethylene and alkenes with the vinyl double bond):

n CH2=CHR → −n−

**Coordination (Ziegler-Natta) Polymerization**

**Early work:**

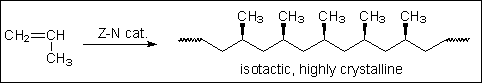
Insertion of aluminum alkyls into olefins was studied by Ziegler:



Important discovery: R3Al + Lewis acids:

Discovery of catalyst

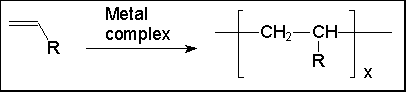
Another important discovery: tacticity control:



Results:

* Nobel Prize in Chemistry for Zeigler and Natta (1963)
* Multibillion $ industry

**Overall Scheme of Coordination Polymerization**



* Limited to ethylene and other a-olefins like propylene. (Actually, it is the only good way to polymerize these monomers.)
* Produces linear polymer, with very few branches (e.g., high density polyethylene, HDPE).
* Capable of producing homo-tactic polymers.
* Most commercial initiators are insoluble complexes or supported on insoluble carriers.
* Very complex mechanism, still poorly understood for the heterogeneous systems.
* Termination is almost exclusively by chain transfer.
* Modern "high mileage" initiators produce up to 1000's of kg per g initiator.
* Initiators are often called "catalysts" even though they are consumed by the process. Many chains are started per molecule of initiator.

**Mechanism of Coordination Polymerization**

The mechanism is poorly understood because it takes place on the surface of an insoluble particle, a difficult situation to probe experimentally. The mechanism shown below is one of several models proposed to at least partially explain the action of the Ziegler-Natta systems, but it is only an approximation of the more complex process that actually occurs.

