# *Olefin Polymerization with Ziegler-Natta Catalyst*

The Ziegler-Natta (ZN) catalyst, named after two chemists: Karl Ziegler and Giulio Natta, is a powerful tool to polymerize α-olefins with high linearity and stereoselectivity (Figure 1). A typical ZN catalyst system usually contains two parts: a transition metal (Group IV metals, like Ti, Zr, Hf) compound and an organoaluminum compound (co-catalyst). The common examples of ZN catalyst systems include $TiCl_4$ + $Et_3Al$ and $TiCl_3$ + $AlEt_2Cl$.

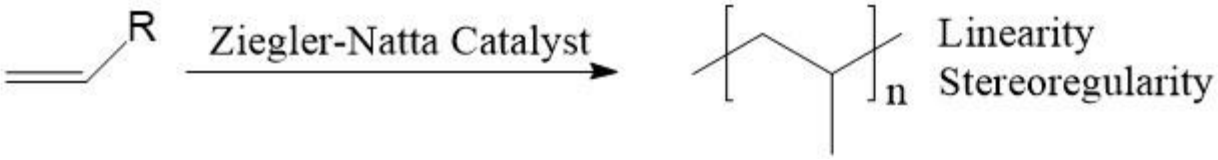


Figure 1: The generic reaction equation for polymerization of -olefins.

In 1953, German chemist Karl Ziegler discovered a catalytic system able to polymerize ethylene into linear, high molecular weight polyethylene which conventional polymerization techniques could not make.[1] The system contained a transition metal halide with a main group element alkyl compound (Figure 2).

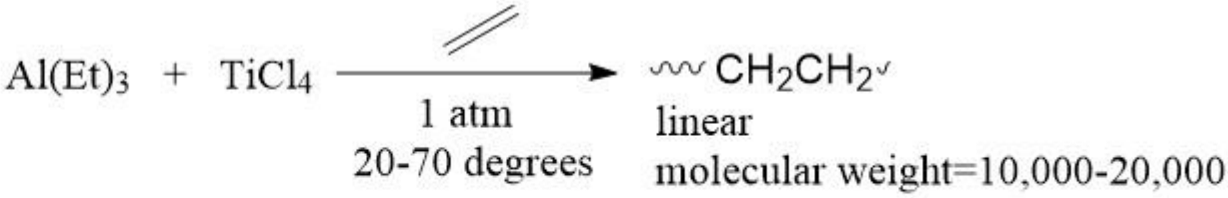


Figure 2: Linear polyethylene obtained by Ziegler's catalytic system (20-70 ).

Following the catalytic design, Italian chemist Giulio Natta found that polymerization of α-olefins resulted in stereoregular structures,[2] either syndiotactic or isotactic, depending on the catalyst used (Figure 3). Because of these important discoveries, Karl Ziegler and Giulio Natta shared the Nobel Prize in Chemistry in 1963.

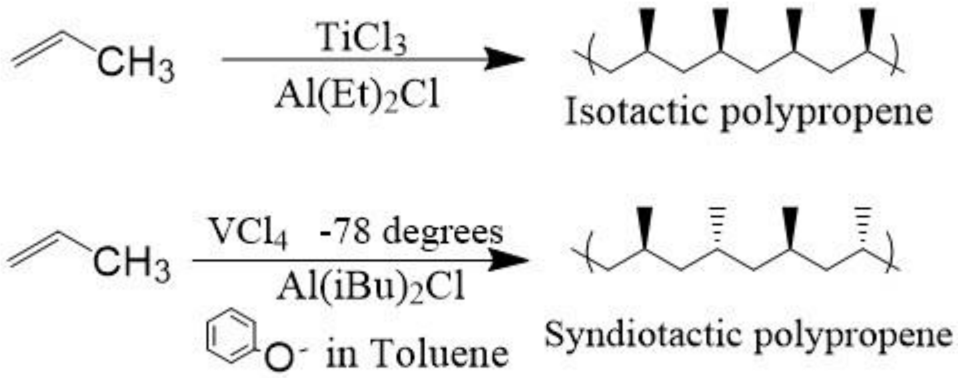


Figure 3: The ZN catalytic polymerization of linear polypropene with two different stereoregular structures.

## Advantages over traditional polymerization method

Traditionally, polymerization of α-olefins was done by radical polymerization (Figure 4). Problem with this technique was that the formation of undesired allylic radicals leaded to branched polymers.[3] For example, radical polymerization of propene gived branched polymers with large molecular weight distribution. Also, radical polymerization had no control over stereochemistry. Linear unbranched polyethylene and stereoregulated polypropylene could not be fabricated by free radical polymerization. This technique largely limited the potential applications of these polymeric materials.

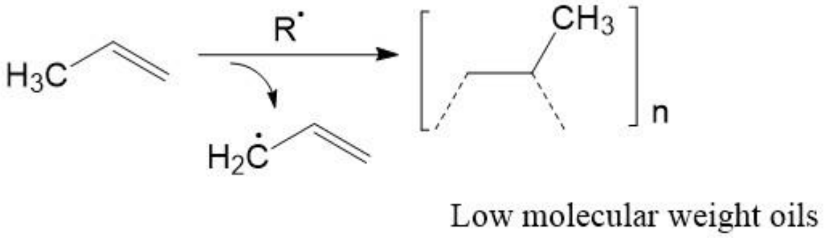


Figure 4: The radical polymerization of propylene using traditional method.

The invention of ZN catalyst successfully addressed these two problems. The catalyst can give linear α-olefin polymers with high and controllable molecular weights. Moreover, it makes the fabrication of polymers with specific tacticity possible. By controlling the stereochemistry of products, either syndiotactic or isotactic polymers can be achieved.

# Mechanism of Ziegler-Natta catalytic polymerization

## *Activation of Ziegler-Natta catalyst*

It is necessary to understand the catalyst's structure before understanding how this catalyst system works. Herein, $TiCl_4$+$AlEt_3$ catalyst system is taken as an example. The titanium chloride compound has a crystal structure in which each Ti atom is coordinated to 6 chlorine atoms. On the crystal surface, a Ti atom is surrounded by 5 chlorine atoms with one empty orbital to be filled. When $Et_3Al$ comes in, it donates an ethyl group to Ti atom and the Al atom is coordinated to one of the chlorine atoms. Meanwhile, one chlorine atom from titanium is kicked out during this process. Thus, the catalyst system still has an empty orbital (Figure 5). The catalyst is activated by the coordination of $AlEt_3$ to Ti atom.

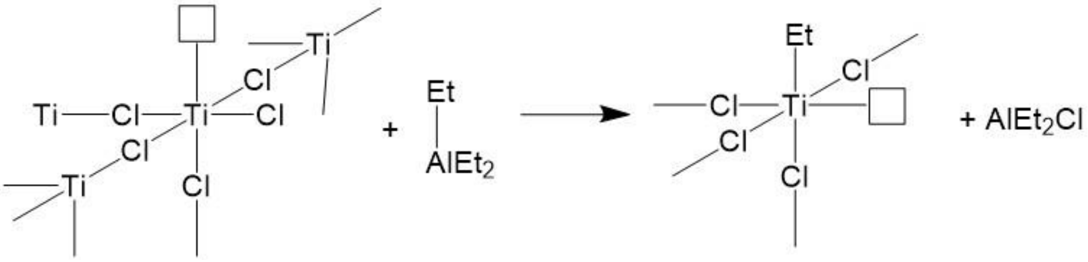


Figure 5: The activation of ZN catalyst system by coordination of $AlEt_3$ to Ti atom.

## *Initiation step*

The polymerization reaction is initiated by forming alkene-metal complex. When a vinyl monomer like propylene comes to the active metal center, it can be coordinated to Ti atom by overlapping their orbitals. As shown in Figure 6, there is an empty dxy orbital and a filled $dx^2$-$y^2$ orbital in Ti's outermost shell (the other four orbitals are not shown here). The carbon-carbon double bond of alkene has a pi bond, which consists of a filled pi-bonding orbital and an empty pi-antibonding orbital. So, the alkene's pi-bonding orbital and the Ti's dxy orbital come together and share a pair of electrons. Once they're together, that Ti’s $dx^2$-$y^2$ orbital comes mighty close to the pi-antibonding orbital, sharing another pair of electrons.

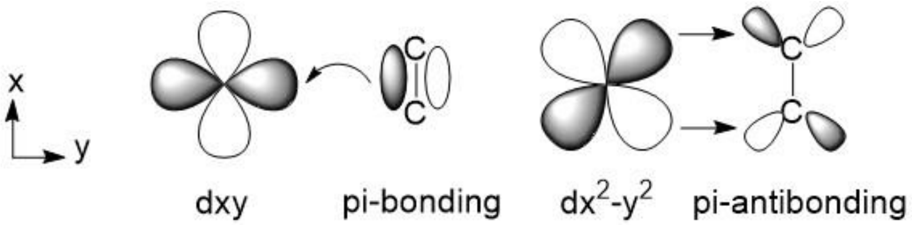
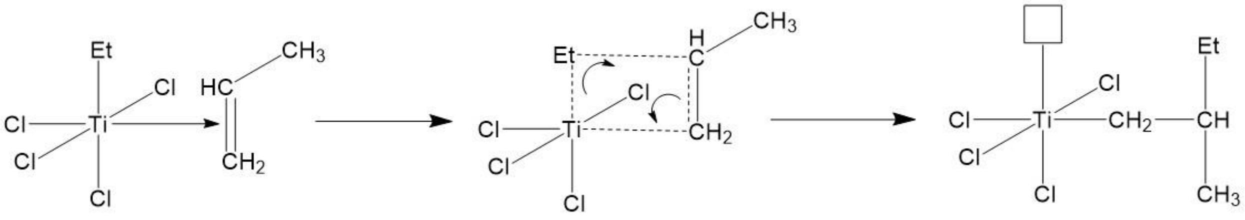


Figure 6: Molecular orbitals representation of monomer coordinating to metal center.

The formed alkene-metal complex (1) then goes through electron shuffling, with several pairs of electrons shifting their positions: The pair of electrons from the carbon-carbon pi-bond shifts to form Ti-carbon bond, while the pair of electrons from the bond between Ti and AlEt3’ ethyl group shifts to form a bond between the ethyl group and the methyl-substituted carbon of propylene (Figure 7). After electron shuffling, Ti is back with an empty orbital again, needing electrons to fill it (2).



1

2

Figure 7: The formation process of alkene-metal complex.

## *Propagation step*

When other propylene molecules come in, this process starts over and over, giving linear polypropylene (Figure 8).

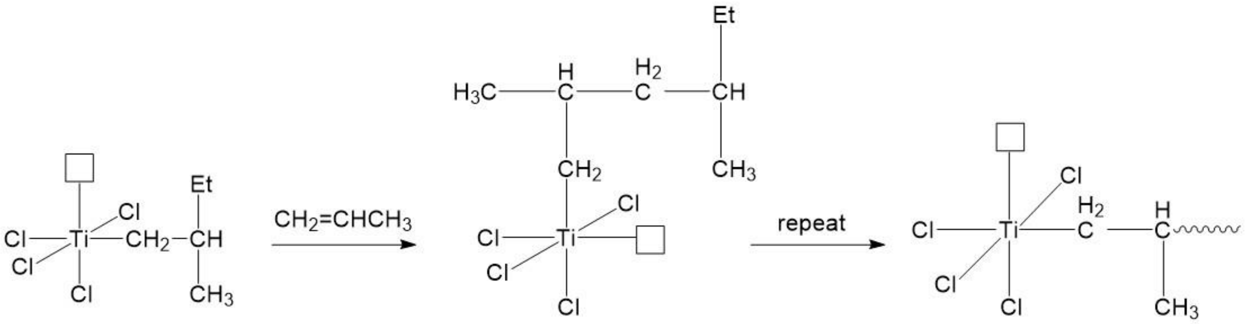
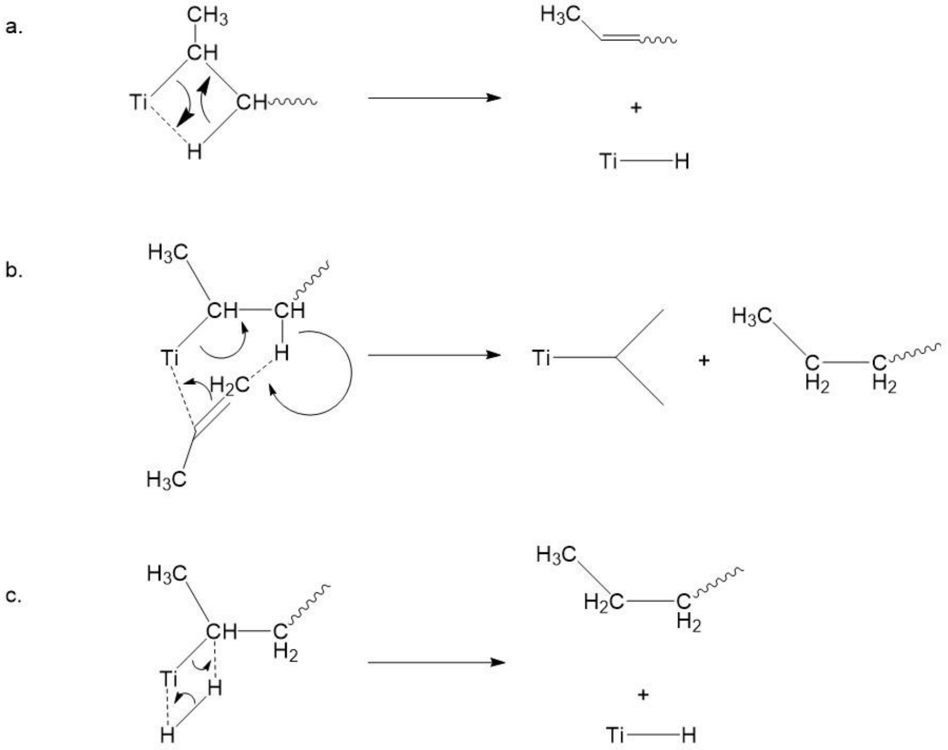


Figure 8: Propagation towards polymeric chains.

### *Termination step*

Termination is the final step of a chain-growth polymerization, forming “dead” polymers (desired products). Figure 9 illustrates several termination approaches developed with the aid of co-catalyst $AlEt_3$.



## *Polymer degradation*

A plastic item with thirty years of exposure to heat and cold, brake fluid, and sunlight. Notice the discoloration, swollen dimensions, and tiny splits running through the material

Polymer degradation is a change in the properties—tensile strength, color, shape, molecular weight, etc.—of a polymer or polymer-based product under the influence of one or more environmental factors, such as heat, light, chemicals and, in some cases, galvanic action. It is often due to the hydrolysis of the bonds connecting the polymer chain, which in turn leads to a decrease in the molecular mass of the polymer. These changes may be undesirable, such as changes during use, or desirable, as in biodegradation or deliberately lowering the molecular mass of a polymer. Such changes occur primarily because of the effect of these factors on the chemical composition of the polymer. Ozone cracking and UV degradation are specific failure modes for certain polymers. The susceptibility of a polymer to degradation depends on its structure. Epoxies and chains containing aromatic functionality are especially susceptible to UV degradation while polyesters are susceptible to degradation by hydrolysis. Carbon based polymers are more susceptible to thermal degradation than inorganically bound polymers such as Polydimethylsiloxane and are therefore not ideal for most high temperature applications.

Polymer degradation may occur through galvanic action. In 1990, Michael Faudree discovered that imide-linked resins in CFRP (carbon fiber reinforced polymers) composites degrade when bare composite is coupled with an active metal in saline, i.e. salt water environments. Polymers affected include bismaleimides (BMI), condensation polyimides, triazines, and blends thereof.

Degradation occurs in the form of dissolved resin and loose fibers. Hydroxyl ions are generated at the graphite cathode attacking the O-C-N bond in the polyimide structure. This phenomenon, that polymers can undergo galvanic corrosion like metals do has been referred to as the "Faudree Effect". Standard corrosion protection procedures were found to prevent polymer degradation under most conditions.

The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. The degradation of polyethylene occurs by random scission—a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When heated above 450 DEGC it degrades to form a mixture of hydrocarbons. Other polymers—like polyalphamethylstyrene—undergo specific chain scission with breakage occurring only at the ends. They literally unzip or depolymerize to become the constituent monomer.

However, the degradation process can be useful from the viewpoints of understanding the structure of a polymer or recycling/reusing the polymer waste to prevent or reduce environmental pollution. Polylactic acid and polyglycolic acid, for example, are two polymers that are useful for their ability to degrade under aqueous conditions. A copolymer of these polymers is used for biomedical applications, such as hydrolysable stitches that degrade over time after they are applied to a wound. These materials can also be used for plastics that will degrade over time after they are used and will therefore not remain as litter.

The sorting of polymer waste for recycling purposes may be facilitated by the use of the Resin identification codes developed by the Society of the Plastics Industry to identify the type of plastic.

## Example

### *Oxidative degradation.*

Oxidative degradation of polymers leads to major changes in their properties.

**Example: oxidation of poly ethylene and poly propylene**