

Coordination Polymerization

Nearly half of all polymers produced worldwide are produced by catalytic polymerization reactions carried out in the presence of transition metal compounds. Coordination of a monomer to a metal center is a crucial step in the catalytic cycle. Therefore, these polymerizations are referred to as “coordination polymerizations”. Especially polypropylene and a large proportion of polyethylene are produced in this way.

Polymerization of α -Olefins

In contrast to many other unsaturated compounds, simple α -olefins cannot be polymerized (with the exception of ethene) via the radical or ionic polymerizations. This is because of the chain carrying the active center—for example, a radical—preferring to abstract a hydrogen atom or an ion from the carbon atom adjacent to the double bond. This results in an allyl species, which is so stable that no other monomer can be added because this would lead to the resonance stabilization being lost. An example of this is the reaction of propene with a source of radicals (**Fig. 1**). The reaction with corresponding anions or cations takes place in an analogous manner. The polymerization of α -olefins only became possible after Karl Ziegler’s discoveries.

Ziegler Catalysts

Karl Ziegler, who was conducting research on the oligomerization of ethene by aluminum alkyls, discovered by accident that transition metals could massively influence this reaction. He noticed that traces of nickel prevented the oligomerization of ethene and that in the presence of nickel only dimers are produced. This effect came to be known as the nickel effect and spurred Ziegler on to analyze more closely the influence of transition metals on oligomerization. During his research he discovered that a mixture of titanium compounds, such as titanium tetrachloride together with aluminum alkyl compounds, could spontaneously polymerize ethene to macromolecular polyethylene at atmospheric pressure and room temperature. At that time this procedure was revolutionary because a typical radical polymerization of ethene, involving a very active primary radical at the growing chain end, required extreme reaction conditions: a temperature of 300 °C and a pressure of up to 2000 bar. In contrast to this, the polymerization using Ziegler catalysts takes place at ambient conditions. To highlight this, Karl Ziegler used a converted preserving jar for presentation purposes.

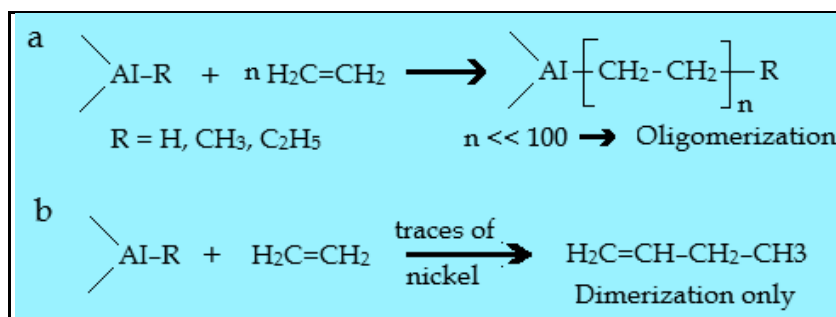


Fig.1: (a) Ziegler's "Aufbaureaktion" (Chain extension reaction). (b) The nickel effect

The reaction takes place with organometallic compounds, formally transition metals, and requires a second component, an aluminum alkyl, as a so-called cocatalyst. Examples are given in the following Table.

Table 1: Examples of Ziegler catalyst and cocatalysts (Et= C₂H₅)

Catalyst	Formula	Cocatalyst	Formula
Titanium tetrachloride	TiCl ₄	Triethyl aluminum	AlEt ₃
Zirconium tetrachloride	ZrCl ₄	Diethyl aluminum chloride	AlEt ₂ Cl
Titanium trichloride	TiCl ₃	Ethyl aluminum dichloride	AlEtCl ₂
Titanium tetraisobutylate	Ti(O-i-C ₄ H ₉) ₄	Diisobutyl aluminum hydride	AlH(i-C ₄ H ₉) ₂
Vanadium oxytrichloride	VOCl ₃		

Heptane or toluene is used as a solvent. The use of metal alkyls dictates strictly anhydrous conditions. Alternatively, traces of water can be scavenged by a surplus of aluminum alkyls. The active catalysts discussed above are insoluble in hydrocarbon solvents and can thus be described as heterogeneous catalysts. The following model is the generally accepted one for Ziegler catalysis and is discussed in the following using titanium tetrachloride as an example. The catalytic cycle can be divided into the basic steps—initiation, growth, chain transfer, and termination—analogueous to other chain growth reactions, such as radical polymerization.

Initiation

Because of the reducing effect of aluminum compounds, the titanium (IV) chloride is reduced and a solid titanium-containing species is formed. On the surface of the solid particles the titanium centers are alkylated by the aluminum alkyl. During this process one of the chloride ions is swapped for an ethyl group. Some of the metal centers on the surface are coordinatively unsaturated and have a free coordination point. The metal atoms are the catalytically active centers (**Fig. 2**).

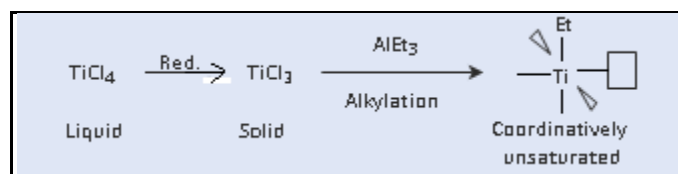


Fig. 2: Initiation process for Ziegler catalysts

Growth

An ethene molecule coordinates with the metal atom via the π -electrons of the double bond as the first part of the growth step. Then an insertion of the ethene molecule over a four-center-four-electron-transition state involving the metal carbon bond already existing takes place. Thus the coordination site that was occupied by the ethyl group becomes available again and so the center is ready for another insertion step (**Fig. 3**). The chain migration during the insertion step leads to a cis-addition (this is known as the chain migratory mechanism). Bi-metallic mechanisms, for example involving chloride bridged titanium–aluminum species, have also been described for chain growth but confirmation has proved difficult because of the heterogeneous nature of the catalytic species.

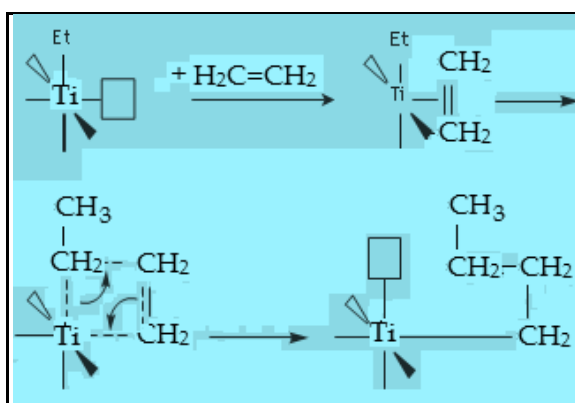


Fig. 3: Chain growth with Ziegler catalysts

Termination/Chain Transfer

Instead of an insertion, the β -carbon of the hydrocarbon chain can be transferred in the form of a hydride ion to the free coordination center or to a coordinated monomer molecule (**Fig. 4**). In both cases an unsaturated polymer is formed. These processes are called β -hydride-elimination or β -hydride-transfer, respectively. The titanium alkyl or titanium hydride species formed during these processes are still active polymerization catalysts and can coordinate with further ethene molecules to initiate new polymer chains.

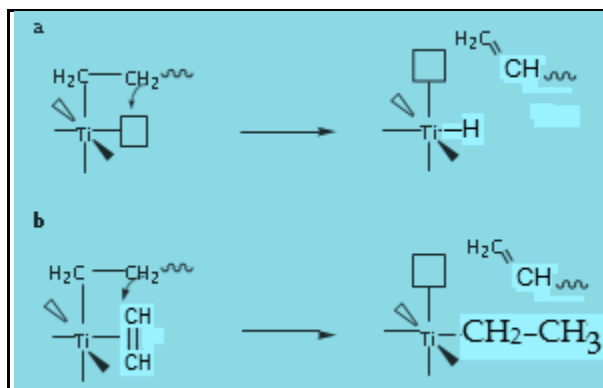


Fig. 4: Chain termination and transfer. (a) Via β -hydride-elimination. (b) Via β -hydride-transfer

It is possible to distinguish between the two mechanisms by varying the ethene concentration, i.e., the ethene pressure above the liquid phase. If termination takes place via β -hydride-elimination then an increase in the ethene concentration increases the rate of chain growth and the rate of termination remains the same. Thus, the molar mass increases with an increase in ethene pressure. If, however, a catalyst system is used, in which a β -H transfer onto a coordinated monomer is favored, an increase in ethene concentration is also beneficial for chain growth and the molar mass is independent of the ethene pressure. Generally, however, both reactions occur concurrently.

Furthermore, termination of the catalytic process can take place because of contamination, by water for example. During catalytic polymerization the molar mass of the polymer is controlled kinetically by the relationship between the rates of chain growth and termination, just as they are during radical or ionic polymerization.

$$\text{Kinetic chain length } \bar{v} = \frac{\text{Olefine insertion rate}}{\text{Rate of } \beta\text{H elimination or transfer}}$$

An increase in the reaction temperature benefits especially the rate of β -H-elimination and β -H-transfer as these reactions have large activation energies. Thus, the polymer molar mass decreases as the reaction temperature are increased. The nickel effect, observed by Ziegler, is attributable to elimination taking place very quickly in the presence of nickel and therefore only a dimerization of the ethene takes place. The molar mass can be regulated by the addition of hydrogen. Molecular hydrogen splits the titanium-alkyl bond (hydrogenolysis). The resulting hydride species can add further monomers so that the rate of polymerization stays the same but shorter polymer chains are formed (**Fig. 5**). The different variants of the Ziegler "Aufbaureaktion" can be summarized in **Fig. 6**.

- Oligomerization of ethene through the “Aufbaureaktion”
- Dimerization of ethene through the nickel effect
- Polymerization of ethene to polyethylene (Muelheim polyethylene low-pressure process)

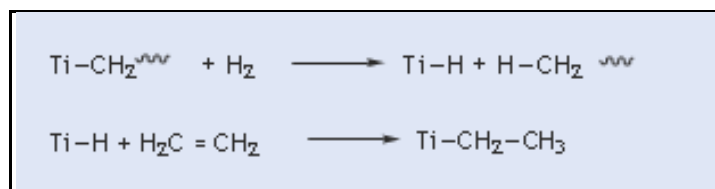


Fig. 5: Regulation of molar mass with hydrogen

The longer chain aluminum alkyls formed during the “Aufbaureaktion” have a narrow molar mass distribution (Poisson distribution) and can be oxidized to alcohols with oxygen. This is a technically used route to valuable raw materials for surfactants. Very pure aluminum oxide is formed as a by-product. As an alternative, olefins can be produced by thermal elimination (Fig. 6).

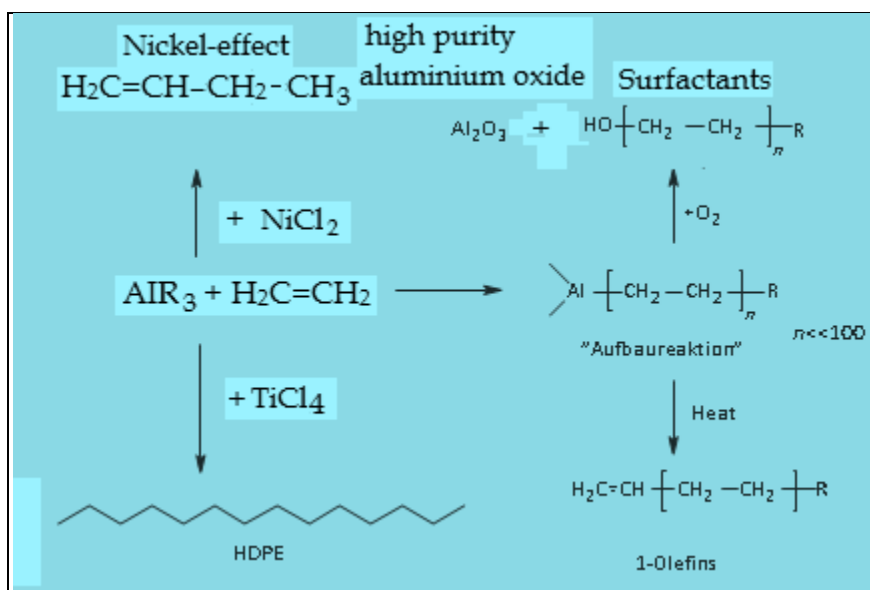


Fig. 6: Reactions of aluminum alkyls with ethene. HDPE high density polyethylene

As well as the systems known as Ziegler catalysts, chrome-based catalysts have also found their way into technical polymerization processes. These systems, known as Phillips catalysts, consist of chromium trioxide on a SiO_2 carrier. Chrome (VI) is probably reduced down to chrome (II) during the reaction. Phillips systems are able to function without a cocatalyst, in contrast to Ziegler catalysts. The mechanism of polyinsertion is suggested to take place in an analogous manner to that described above

for titaniumbased catalysts. As a group, the reactivity of these systems is somewhat lower than that of Ziegler catalysts so that higher temperatures and higher olefin pressures are necessary and, usually, polymers of low molar mass are produced. Processes based on these catalysts are referred to as medium-pressure processes. The differences are summarized in **Table 2**.

Table 2. A comparison of the process parameters for low and medium pressure processes		
Process	Low pressure	Medium pressure
Catalyst	TiCl ₄ /AlR ₃	CrO ₃ /SiO ₂
<i>p</i> (bar)	1-10	35
<i>T</i> (°C)	70	150-180
<i>M_w</i> (kg/mol)	50-100	5-20

As early as 1 year after their discovery, the applicability of the titanium catalysts discovered by Ziegler was substantially broadened by the Italian scientist Giulio Natta. Natta discovered that the systems described by Ziegler could polymerize not only ethene but also higher α -olefins. The polypropylene produced using the first generation of, not yet optimized, Ziegler catalysts was essentially atactic or stereo-irregular and thus soluble in the reaction medium. No precipitated polymer could be observed during the reaction, in contrast to insoluble polyethylene, which is probably why this important discovery was overlooked in Karl Ziegler's laboratories.

Karl Ziegler and Giulio Natta received the 1963 Nobel Prize for Chemistry for the discovery of the catalytic polymerization of α -olefins and the stereospecific polymerization of propene.