Kinetics of Polymerization: D] Coordination addition polymerization:

The field of coordination polymerization originated in the mid-1950s with the pioneering works of Karl Ziegler in Germany and Giulio Natta in Italy. While Ziegler discovered in the early 1950s that a combination of aluminum alkyls with certain transition metal compounds such as TiCl₄ or VCl₄ generated complexes that would polymerize ethylene at low temperatures and pressures producing polyethylene with an essentially linear structure, now referred to as high-density polyethylene (HDPE), Natta’s work led to the recognition that the catalytic complexes described by Ziegler were capable of polymerizing 1-alkenes (commonly known as alpha olefins in the chemical industry) to yield stereoregular polymers. For example,

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Reaction condition</th>
<th>Polymer structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>TiCl₄, Et₃Al in n-heptane, 50°C</td>
<td>isotactic</td>
</tr>
<tr>
<td>Me</td>
<td>VCl₄, Et₃Al, PhOMe in toluene, -78°C</td>
<td>syndiotactic</td>
</tr>
</tbody>
</table>

The range of this type of catalysts, referred to as Ziegler-Natta (ZN) catalysts, was subsequently extended to produce polymers exhibiting a wide range of stereoregular structures including those derived from dienes and cycloalkenes. Many polymers are now manufactured on a commercial scale using Ziegler-Natta catalysts, the most prominent among them being stereoregular (isotactic) polypropylene of high molecular weight. (Recall that propylene cannot be polymerized by either free radical or ionic initiators.) Ziegler and Natta received the 1963 Nobel prize in chemistry jointly in recognition of the scientific and practical significance of their work.

Since the Ziegler-Natta catalyst systems appear to function via formation of a coordination complex between the catalyst, growing chain, and incoming monomer, the process is also referred to as coordination addition polymerization and the catalysts as coordination catalysts or coordination initiators. The terms isoselective and syndioselective are used to describe initiators and polymerizations that produce isotactic and syndiotactic polymers, respectively. Other types of complex catalysts that have received attention for stereospecific polymerization are the reduced metal oxides and the alfin catalysts (prepared from compounds of sodium). All three types are mainly used in heterogeneous polymerization, although some homogeneous processes are also used. Metallocene-based ZN catalysts appeared on the scene in the early 1980s. Compared to conventional heterogeneous ZN systems in which a variety of active centers with different structures and activities usually coexist, homogeneous metallocene-based catalysts have very uniform catalytically active sites which possess controlled, well-defined ligand environments, thus allowing much greater control on the polymer formed.

ZN catalysts: Catalyst composition

The work of Ziegler and Natta led to the development of a very large number of two-component initiator systems consisting of an organometallic compound or hydride of a group I–III metal together with a halide or other derivative of a group IV–VIII transition metal. The more important component of the initiator system is the transition metal compound. The function of the group I–III metal compound is to modify and activate the transition metal compound for initiation. The transition metal compound is referred to as the catalyst and the organometallic compound as the co-catalyst. A combination of the
catalyst and the cocatalyst is often referred to simply as the catalyst. The catalyst component usually consists of halides or oxoaldehydes of titanium, vanadium, chromium, molybdenum, or zirconium, and the co-catalyst component often consists of an alkyl, aryl, or hydride of metals such as aluminum, lithium, zinc, tin, cadmium, beryllium, and magnesium. The catalyst systems may be heterogeneous (some titanium-based systems) or soluble (most vanadium containing species). The best known systems are probably those derived from TiCl₄ or TiCl₃ and an aluminum trialkyl. These initiator systems are the traditional Ziegler–Natta initiators. The catalysts which are useful for the preparation of isotactic polymers are heterogeneous, i.e. they are insoluble in the solvent, or diluent, in which they are prepared. They are prepared by mixing the components in a dry, inert solvent such as hexane in the absence of oxygen, usually at a low temperature.

Mechanism of stereoselective placement:

It is generally agreed that the heterogeneous Ziegler-Natta polymerization occurs at localized sites on the catalyst surface, which are activated by the organometallic component by alkylation of a transition metal atom at the surface. In polymerization with Ziegler-Natta catalysts, a radical mechanism is not acceptable as it cannot explain the stereoregularity and formation of isotactic polymers. An ionic mechanism is, of necessity, widely favoured and accepted. Coordination initiators perform two functions. First, they supply the species that initiates the polymerization. Second, the fragment of the initiator residue from the initiating portion has unique coordinating powers. Coordination of this fragment (which may be considered as the counterion of the propagating center) with both the propagating chain end and the incoming monomer occurs so as to orient the monomer with respect to the growing chain end and bring about stereoselective addition.

Stereoselective polymerization is a concerted, multi-centered reaction. The figure below depicts the general situation for an anionic coordination polymerization proceeding with isotactic placement. The polymer chain end has a partial negative charge with the initiator fragment G (the counterion or the gengenion) having a partial positive charge (a cationic coordination polymerization involves a similar mechanism except for reversal of the signs of the partial charges.) The initiator fragment G is coordinated with both the propagating chain end and the incoming monomer molecule. The stereospecific polymerization of α-olefins and other nonpolar alkenes proceeds by π-complexation between monomer and the transition metal in G, followed by insertion of a monomer molecule into the metal-carbon bond by a four-center anionic coordination insertion process, permitting head-to-tail addition and hair-like growth on the anionic site.

The monomer is oriented and “held in place” by coordination during addition to the polymer chain. Coordination between the initiator fragment and the propagating centre is broken simultaneously with the formation of bonds between the propagating centre and the new monomer unit and between the initiator fragment and the new monomer unit. Propagation proceeds in the four-center cyclic transition state by the insertion of monomer between the initiator fragment and the propagating center. The initiator fragment essentially acts as a template or mold for the successive orientations and isotactic placements of the incoming monomer units. Isotactic polymerization occurs because the initiator
fragment forces each monomer unit to approach the propagating centre with the same face. This mechanism is referred to as catalyst (initiator) site control or enantiomorphic site control. For the polymerization described in this figure above, monomer approaches the propagating centre with its re face facing the propagating centre.

The description in the preceding figure for isotactic polymerization could also have been shown with the R and H groups of the last monomer unit in the polymer chain reversed (R in back and H in front), in which case isotactic propagation consists of monomer always approaching the propagating center with its si face.

The property of the initiator fragment that forces successive placements of monomer to occur with the same face is chirality. There is a stereochemical "fit" between initiator and monomer, which overrides the usual tendency toward moderate syndiotacticity. The initiator in isotactic polymerization is usually a racemic mixture of two enantiomers. One of the enantiomers yields isotactic polymer by forcing all propagations via the Re face of monomer; the other enantiomer, via the Si face. The isotactic polymer structures formed from the enantiomeric initiators are the same polymer; that is, they are superposable (ignoring the effects of end groups) for most monomers.

**Mechanism of ZN polymerisation:**

Out of the several proposed pathways, here we will discuss the one put forward by Cossee and Arlman. We will use TiCl$_5$ / Et$_2$AlCl combination as the ZN catalyst. But before we go into the details, it helps to know about the structure of TiCl$_5$. The structural variant that is used here with most success is the $\alpha$-TiCl$_5$. In its crystal structure, each Ti is surrounded by six chlorines in an octahedral arrangement.

This is what the arrangement is inside the crystal, but at the surface each Ti is surrounded by only five chlorine atoms, leaving one coordination site unoccupied.
The blue Ti on the interior of the crystal has six Cl atoms around itself, but the red Ti on the surface has only five. It is at this position the reaction will happen. The surface Ti atom will be represented in the following way from now on:

The organoaluminium supplies one of its ethyls to the impoverished Ti atom but in doing so also knocks off one of the Cl atoms. The result is Ti still has one vacant coordination site.

The still vacant coordination site of Ti is now filled by the olefin monomer which forms a complex with the metal centre by donating its electrons from the $\pi$-MO into one of the vacant d orbitals of the metal. The metal also donates electrons from one of its filled d-orbitals into the vacant $\pi^*$-MO (antibonding), making the complex stronger:

The precise nature of the complex formed between the olefin and the metal is complicated. We choose to represent it in a simplified way:

Ti-propylene complex
The olefin will now insert itself into the metal alkyl bond (migratory insertion) via a four-membered TS and in doing so, creates a vacant coordination site on Ti:

The C-C-C chain now migrates to its original position with regeneration of the original configuration of the vacant site, often referred to as backskip or back-flip.

The second monomer now approaches the vacant coordination site on Ti, and the whole process is repeated.
This means that for each monomer incorporation, the polymer chain migrates *twice*. Once during the migratory insertion, and again during the back-flip. The overall process can be regarded as *site epimerization*.

A variation on this mechanism involves a lowering of the transition state barrier to insertion by an α-agostic interaction, specifically, an attractive interaction between titanium and a hydrogen on the first carbon attached to Ti. This helps to tilt the localized sp³ alkyl orbital (in the growing polymer chain) away from the metal and more toward the olefin ligand to promote the migratory insertion.

The distinctive characteristic of Ziegler-Natta catalysts is their ability to produce stereoregular polymers. To obtain a stereoregular polymer, according to the Cossee-Arelman mechanism, the chemisorption of the monomer should always lead to the same orientation of the molecule on the catalyst surface. It becomes apparent from an examination of models that a molecule such as propylene can fit into the catalyst surface in only one way if a position of closest approach of the double bond to the Ti³⁺ ion is to be achieved. This requires that the CH₂ group of the incoming monomer points into the lattice and, consequently, *for steric reasons* the orientation of the CH₂ group to one side is preferred. It thus ensures that the configuration of the monomer while complexing at the vacant site, prior to incorporation into the polymer chain, is always the same so that an isotactic polymer is formed. Since migration of the vacant site back to its original position is necessary for isospecific polymerization, this also implies that the tacticity of the polymer formed depends essentially on the rates of both the alkyl shift and the migration. Since both these processes slow down at lower temperatures, a syndiotactic, instead of isotactic, polymer would be formed when the temperature is decreased. In fact, syndiotactic polypropylene can be obtained at 70°C.

Recall that with vanadium catalyst, the polymerization is in fact syndioselective. With VCl₄, AlEt₂Cl, we get syndiotactic polypropylene. Presumably, this difference arises due to the fact that for the vanadium catalyst system, the back flip *does not* take place. The reaction is believed to proceed in the following way (we start from the Al-activated vanadium catalyst):
The termination steps may involve β-hydride transfer to either the transition metal or the monomer, or chain transfer to an active hydrogen compound such as molecular hydrogen or to the group I-III metal alkyls:

1. \[
\begin{align*}
\text{Me} & \quad \text{H} \\
\text{Me} & \quad \text{H} \\
\text{Me} & \quad \text{H} \\
\end{align*}
\] \[\text{Ti} - \text{H} \quad + \quad \text{H} - \text{Me} \]

2. \[
\begin{align*}
\text{Me} & \quad \text{H} \\
\text{H} & \quad \text{Me} \\
\text{Me} & \quad \text{H} \\
\end{align*}
\] \[\text{Me} - \text{H} \quad + \quad \text{Ti} - \text{H} \quad \rightarrow \quad \text{Me} - \text{Ti} \quad + \quad \text{H} - \text{Me}\]

(The methylene carbon from monomer regioselectively binds to the Ti)

3. \[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{Me} & \quad \text{H} \\
\text{Me} & \quad \text{H} \\
\end{align*}
\] \[\text{H} - \text{Ti} \quad + \quad \text{H} - \text{Me}\]

(isopropyl end group)
4. \[ \text{Et}_2\text{AlEt} + \text{Ti} \rightarrow \text{Et} - \text{Ti} + \text{Et}_2\text{AlEt} \]

(Hydrolytic workup of the polymer cleaves the aluminium-polymer bond to yield an isopropyl end group.)

The $\beta$-hydride transfer reactions produce polymers with one saturated and one unsaturated end group. The other two transfers result in polymers with two saturated groups. The chain-breaking reactions limit the polymer molecular weight, but like typical chain transfer reactions, they proceed with the re-initiation of new propagating chains. The extents to which the various chain-breaking reactions occur depend on the monomer, identity and concentrations of the initiator components, temperature, and other reaction conditions. The $\beta$-hydride transfer reactions are usually the predominant chain-breaking reaction in the absence of $\text{H}_2$ or other active hydrogen compound. $\text{H}_2$ is a highly effective chain-transfer agent and is used for molecular weight control in commercial polymerizations of ethylene and $\alpha$-olefins.

**Kinetics of coordination polymerization: ZN polymerization**

The kinetics of Ziegler–Natta polymerization are complex. The relatively few polymerizations that are homogeneous behave in a manner generally similar to non-coordination ionic polymerizations. The heterogeneous systems usually exhibit complicated behaviour as shown in the following figure.

The behaviour described by plot 1 is usually observed when the particle size of the transition metal component is relatively large. The particles of the transition metal component consist of aggregates of smaller crystals. The mechanical pressure of the growing polymer chains cleaves these aggregates with the result that the initiator surface area, number of active sites, and polymerization rate increase with time. After this initial period, referred to as a *buildup* or *settling* period, a steady-state rate is reached, which corresponds to cleavage of the initial particles to the smallest-sized particles. When the initial particle size is decreased (by ball milling), the time required to reach the steady-state polymerization rate is decreased (plot 2). Other factors responsible for the buildup period include the time needed for the formation of the active sites by reaction of the two metal components, slow initiation, and the presence of impurities. Most of these factors are moderated for the typical situation where the initiator system is preformed and allowed to age prior to use in initiating polymerization. The superactive supported initiators often show very little or no buildup period.

Many polymerizations show a settling period with a relatively rapid rise in rate to a maximum value followed by a decay to the steady-state rate (plot 3). This behavior indicates the presence of active sites of differing activities with some of the active sites decaying with time. This behavior is avoided in some instances by aging the initiator. Ziegler–Natta polymerizations may exhibit a continuous rate decrease (plot 4) after the settling period (which may be of either type 1, 2, or 3) due to active site destruction. This can be due to thermal deactivation or further reduction of the transition metal by the group I-III metal component. Diffusion control of the propagation reaction has also been postulated. Diffusion of the monomer through the formed polymer to the propagation centers may become rate-
determining at higher conversions. This has been substantiated in some systems where the polymerization rate increases with increased rate of stirring, but data in other systems indicate diffusion control to be absent.

Homogeneous kinetics are applicable to some Ziegler–Natta polymerizations, when adsorption of initiator components or monomer is not important. The polymerization rate is expressed as:

$$R_p = k_p[C^*][M]$$

where $[C^*]$ is the concentration of active sites expressed in moles per liter.

Adsorption phenomena are important in most Ziegler–Natta polymerizations, and this requires treatment by heterogeneous kinetics. A number of kinetic schemes have thus been proposed based on the assumption that the polymerization centers are formed by the adsorption of metal alkyl species on to the surface of a crystalline transition metal halide and that chain propagation occurs between the adsorbed metal alkyl and monomer. In this regard the Rideal rate law and the Langmuir–Hinshelwood rate law for adsorption and reaction on solids assume importance. The exact form of the resulting kinetic expressions differs depending on the specific adsorption phenomena that are important in the particular reaction system.

Consider a Langmuir–Hinshelwood model where reaction occurs only after monomer is adsorbed from solution onto the transition metal active sites. Further, we assume that the group I–III metal component (A) is present in solution and competes with monomer (M) for the same sites; that is, there is excess group I–III metal component over and above the amount needed to activate (reduce/alkylate) the transition metal sites. The fraction $\Theta_A$ and $\Theta_M$ of the transition metal sites covered with the group I–III metal component and monomer, respectively, are given by:

$$\Theta_A = \frac{K_A[A]}{1 + K_A[A] + K_M[M]}$$

$$\Theta_M = \frac{K_M[M]}{1 + K_A[A] + K_M[M]}$$

where [A] and [M] are the concentrations of the group I–III metal component and monomer in solution, respectively, and $K_A$ and $K_M$ are the respective equilibrium constants for their adsorption.

Propagation occurs by reaction of adsorbed monomer at the active sites at a rate given by:

$$R_p = k_p[C^*]\Theta_M = \frac{k_p[C^*]K_M[M]}{1 + K_A[A] + K_M[M]}$$

If the group I–III metal component does not compete with monomer for the active sites, then

$$K_A[A] = 0$$

Then,

$$R_p = \frac{k_p[C^*]K_M[M]}{1 + K_M[M]}$$

The degree of polymerization is obtained by dividing the propagation rate by the sum of all chain-breaking (transfer) reactions. For the simple situation where the only $\beta$-hydride transfer is that described by termination pathway 1 and 2 (which produce vinylidene end groups in polypropene) and no $\beta$-alkyl transfer occurs, the degree of polymerization is:
\[
\frac{1}{\bar{X}_n} = \frac{k_{\text{tr},M}}{k_p} + \frac{k_s}{k_p K_M[M]} + \frac{k_{\text{tr},K}[A]}{k_p K_M[M]} + \frac{k_{\text{tr},H_2}[H_2]}{k_p K_M[M]}
\]

Where \(k_{\alpha,M}\) is the rate constant for \(\beta\)-H transfer to monomer, \(k_s\) is the rate constant for \(\beta\)-H transfer to the transition metal and \(k_{\text{tr},H_2}\) is the rate constant for chain transfer to molecular hydrogen.

**Recommended texts:**