CHAPTER I I I

THEORY

The stereospecific polymerization of propylene by Natta in 1954 was a scientific breakthrough with immediate industrial significance. By obtaining the alignment of propylene molecules, a crystalline polymer, isotactic polypropylene, was synthesized at high yields in a manner that could be exploited commercially. This achievement, which spurred interest in organometallic chemistry, as well as in polymerization, was recognized by the award of the 1963 Nobel prize in chemistry to Natta and Ziegler, who discovered the basic catalyst system for polymerizing ethylene [54].

Interest in isotactic polypropylene was so high that only three years elapsed between the laboratory discovery and the first commercial production. The excellent combination of thermal and mechanical properties was quickly exploited in a variety of applications, such as injection molding and film and fiber production. This versatility, combined with favorable economics, encouraged a rapid expansion in the use of this material in the 1960s and the early 1970s. At present, polypropylene is one of the most important commercial thermoplastics; its consumption is still increasing more rapidly than the total for all thermoplastics. This situation is likely to continue into the future for the following reasons:

1. The relatively low cost of the product is due to low monomer cost and efficient polymerization technology, compared with other thermoplastics. Competition in licensing technology and production methods promotes further cost reduction by technical improvements.

2. The polymer can be modified for a variety of applications. Through copolymerization, orientaiton, and other techniques the physical properties of the product can be varied to meet a wide range of thermal and mechanical requirements.

3. The ease in processing these polymers allows their economic use in most commercial fabrication techniques. Modifications of the melt rheology increase this versatility [54].

3.1 PURITY

Purity is important in polymerization, with specifications becoming more and more stringent because of the effects of even traces of poisons. Impurities may be classified into inert and copolymerizable components and poisons.

Inert components include propane, ethane, methane, nitrogen, and higher saturated hydrocarbons. They act as diluents, reducing polymer yield. In the presence of highly active catalysts and high monomer concentration, limited amounts may be tolerated. Copolymerizable components, e.g., ethylene and butenes, may be allowed up to the point at which their concentration is high enough to affect properties when incorporated in the polymeric chain.

Catalyst poisons may vary according to quantity and quality as a function of both the process for the production of monomer and the feedstock used. Significant poisons are acetylene, dienes, CO, CO_2, oxygen, water, alcohols, H_2S, carbon oxysulfide (COS), and sulfur-containing components. The effect on catalyst performance depends on the type of catalyst and (to a lesser extent) the process used. Specifications covering the use of $TiCl_3$-based or $MgCl_2$-supported catalysts are reported in Table 3.1, 3.2 and 3.3. The poisons affect catalyst activity, stereospecificity, and polymer morphology.

Molecular sieves and alumina are used to remove poisons such as water and CO_2. In other methods, selective hydrogenation decreases acetylenic and dienic products, and CO is oxidized to CO_2 with Cu and Zn oxides. COS is removed by sodium hydroxide or hydrogen by converting it to H_2S and CO. H_2S is adsorbed on metallic oxides. High concentrations of aluminum alkyl catalyst reduce water, alcohol, and CO_2 production [54].

Table 3.1 Propylene Specifications for Polymerization with $TiCl_3$ - based Catalyst

Propylene concentration, %	Chemical grade			Polymerization grade		
	Minimum 90	Typical 92	Maximum 95	Minimum 99.7	Typical 99.8	Minimum 99.8
impurities, ppm maximum						
ethylene	500	300	50	50	20	5
butylene	500	500	50	50	20	10
C4 hydrocarbon		200	100			
saturated hydrocarbons	5000	1500	1500	1000	200	200
total unsaturated hc.	100	100	100			
butadiene	20	20	20	10	5	3
methylacetylene	10	10	5	10	10	5
propadiene	50	10	10	10	5	3
sulfur	5	5	2	5	5	2
O_2 and N_2	10	5	2	10	10	5
CO	5	5	5	10	5	3
CO_2	10	10	10	5	5	5
N_2O	20	20	20	5	5	2
H_2				20	5	1
methanol					5	
heavy hydrocarbon	1500	1000	500			

Table 3.2 Specifications for Monomer Purity Used in Gas-phase Polypropylene Polymerization, TiCl₃ Catalyst[54]

Components	Mininum	Maximum
monomers, mol %		
propylene	99.5	
propane		0.5
methane and ethane		0.04
traces, ppm		
ethylene		45
acetylene, methyl-acetylene, propadiene		6
C_4		10
CO		5
CO_2		5
O_2		5
H_2		10
H_2O		10
S (as H_2S)		2
CH_3OH		5

Table 3.3 Impurities Specifications for Propylene Polymerization with $MgCl_2$ supported Catalyst[54]

Impurity, vol ppm	Maximum
butadiene	10
allene	5
methylacetylene	5
oxygen	2
carbon monoxide	0.3
carbon dioxide	5
water	5
COS	0.03
total sulfur	1
methanol	5
C_6-C_{12} hydrocarbons	20

3.2 MOLECULAR STRUCTURE
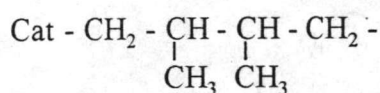
In polymerization with Ziegler-Natta catalysts, propene or longer-chained α-olefins are inserted into the growing chain in a head-to-tail fashion with high selectivtiy. Every CH_2 group (head) is followed by a $CH(R)$ group (tail) with a tertiary carbon atom bearing a methyl or even larger alkyl group:

$$Cat - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - \underset{\underset{CH_3}{|}}{CH} -$$
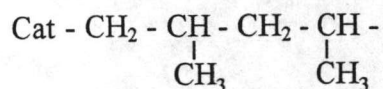
This construction principle is mandatory for the stereoregular structure of the polypropylene molecule. In addition, head - to - head

$$Cat - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - \underset{\underset{CH_3}{|}}{CH} -$$

and tail - to - tail

$$Cat - CH_2 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_2 -$$
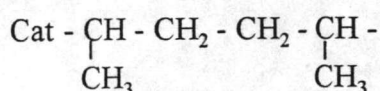
arrangements can occur. These links can be detected by bands at 750 and 112 cm^{-1} in their infrared spectra. Exclusive head - to - tail bonding is a mandatory but not a sufficient condition for stereoregularity. Another important detail is the sterical orientation of the pendant methyl groups with respect to the main C-C axis of the polymer molecule.

Natta formulated three different structures (Figure 3.1) :

1. In the structure all pendant methyl groups are located on one side of the zigzag plane; these polymers are called isotactic.

2. For polymers in which the position of the pendant methyl groups is alternatingly above and below the backbone plane, the term syndiotactic is used.

3. When the pendant methyl groups are randomly positioned above and below the plane, the polymer is said to be atactic. [54]

Isotactic structure
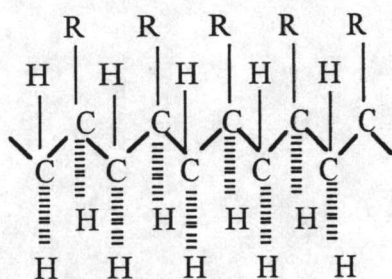
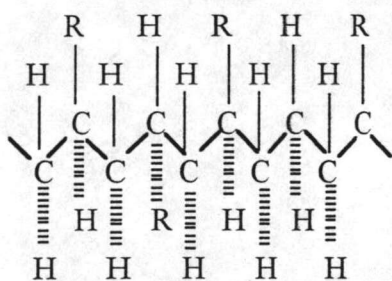Syndiotactic structure
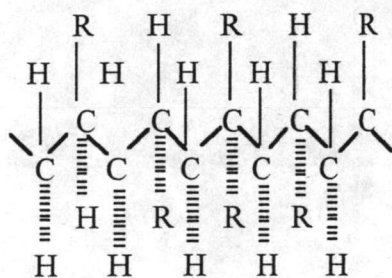
Atactic structure

Figure 3.1 Planar representation of chains of polpropylene(– ,in plane of paper; –
above plane of paper; ▥,below plane of plane)

The tertiary carbon atoms in polyalkene chains are not strictly asymmetric since two substituents are constructed from infinite monomer sequences, and are thus similar, and so the symbols of asymmetric carbon atoms, R and S, can not be usefully applied. Normally the symbols D and L are used to designate the two possible configurations of the tertiary carbon atoms in polyalkene chains: DDDDDDD or LLLLLLL, an isotactic sequence; DLDLDLDL, a syndiotactic sequence; DLDDLDDDLLDLLLDDDDLL, an atactic sequence.

In reality the polymer chain never adopts the flat extended forms shown in Figure 3.1 but is coiled in a helix since such a structure results in the least crowding between the hydrogen atoms. Helical structures for isotactic and syndiotactic polypropylene are shown in Figure 3.2.

The polymerization of propylene by heterogeneous Ziegler-Natta catalysts produces a mixture of isotactic and atactic polymer, and one of the many significant contributions made by Natta and his co-workers was a rapid method they devised for polymer characterization which was based on simple stereoisometric fractionation procedures involving the use of boiling solvents, e.g. ether, heptane, xylene, etc. However, different solvents tend to extract varying fractions of lower molecular weight material, as well as removing atactic polymer. The most common procedure adopted in industrial laboratories is extraction using boiling n-heptane, and the percentage of polymer insoluble in this solvent under these conditions is normally referred to as the Isotactic Index (II). It should, however, be realized that the term atactic is used loosely since the soluble fraction may contain chains made up of blocks of isotactic or syndiotactic placements in addition to purely atactic material [54].

The properties of isotactic, syndiotactic, and atactic polypropylene are given in Table 3.4 Syndiotactic polypropylene is of a more scientific than practical interest. Furthermore, it is difficult to synthesize (particularly because of the required temperature of -70°C) [53].
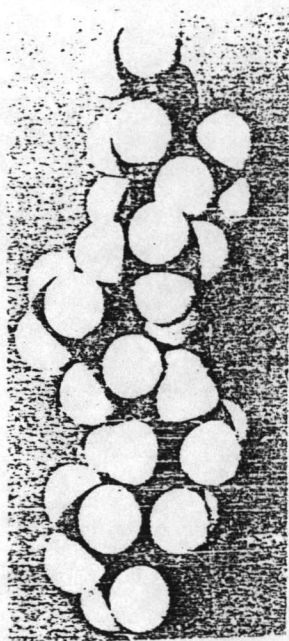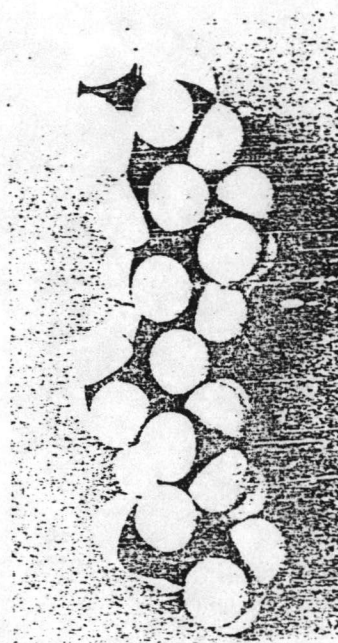
(a)   (b)

Figure 3.2 Chain models of helices of (a) isotactic and (b) syndiotactic
polypropylene

Table 3.4 Properties of Isotactic, Syndiotactic, and Atactic Polypropylene [54].

Property	Isotactic	Syndiotactic	Atactic
density, g/cm^3	0.92-0.94	0.89-0.91	0.85-0.90
melting point, ^oC	165	135	-
solubility in hydrocarbons at 20 ^oC	none	medium	high
yield strength	high	medium	very low

3.3 DEFINITION OF ZIEGLER-NATTA CATALYST

Ziegler-Natta catalysts are broadly defined in terms of their preparation which involves reacting compounds (commonly halides) of groups IV - VIII transition metals (e.g. Ti, V, Cr, Zr) with organometallic compounds (e.g. alkyls, aryls or hydrides) of groups I - III metals (e.g. Al, Mg, Li) as shown below. This definition is in fact too broad since not all such reactions yield catalysts suitable for preparing stereoregular polymers. Nevertheless, for each monomer there is a wide range of catalysts that are suitable [55].

Transition metal   +   Metal alkyl, aryl, ⟶ Active Ziegler-
    compound   or hydride   Natta catalyst
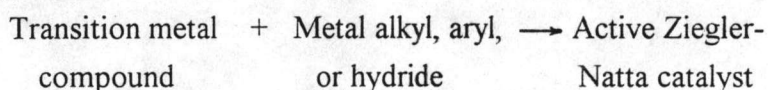
The type of solvent of diluent should not be omitted in reporting a catalyst system. Ziegler-Natta polymerizations are usually carried out in inert solvents, e.g. heptane or toluene. The use of polar solvents can drastically alter the reaction mechanism. Both monomer and diluent or solvent must be clearly specified in defining a particular Ziegler-Natta catalyst system [54].

3.4 FACTORS DETERMINING BEHAVIOR OF CATALYSTS

Activity, stereoregulating ability, and selectivity to form stereochemical configuration are elucidated in term of "behavior". The factors described are

related to the chemical structure of the metal alkyl (organometallic compound also designated) and the transition metal salt.

3.4.1 The Metal Alkyls

3.4.1.1 Group of Metal

Not every metal in groups I to III forms as active metal alkyl an claimed in many of the patents relating to Ziegler-Natta catalysts. Active catalysts from the following metals have been established for ethylene and propylene polymerization.

Table 3.5 Group of metal in metal alkyls

Group I	Group II	Group III
Li	Be	Al
Na	Mg	Ga
K	Zn	
	Cd	

Of these, aluminum alkyls have been the most extensively used, and the reason for this is partly scientific and partly economic. By the end of 1950's, aluminum alkyls such as $AlEt_3$ and $Al-i-Bu_3$, became available in research and developmental quantities in the pure state or in hydrocarbon solutions. Facile synthetic methods were developed using Al, H_2, and olefin. They were much safer to use in solution because, once properly diluted, they were less pyrophoric or not flammable unless contacted with a combustible material. Simple syringing technique, using N_2 or Ar as an inert atmosphere, became widely used to dispense metal alkyl solutions. Eventually, many different aluminum alkyls became commercially available, and with modest precaution they could be used safely and routinely in research work by persons with little experience.

The most important impetus, however, was the discoverying that all of the desired stereoregular polymers could be made by a proper selection of an aluminum alkyl and a transition metal salt. The marriage of these factors has probably made aluminum alkyls the choice metal alkyl component in most, if not

all, commercial processes. The most widely used aluminum alkyls have been AlEt$_3$, AlEt$_2$Cl, AlEtCl$_2$, and AlEt$_2$OR. Binary complexes of lithium alkyls and aluminum alkyls, such as LiAlR$_4$ have also been explored.

Of the other metals of group III, only gallium is attractive, but its high cost has prevented extensive examination. Tanaka and co-workers have found that the catalytic activity of GaR$_3$-TiCl$_4$ catalysts in the low pressure polymerization of ethylene was lower compared with catalysts containing analogous aluminum alkyls [55]. The order of activity : GaPr$_3$ > GaMe$_3$ > GaEt$_3$ was found.

Of the group I metals, metal alkyls from lithium, sodium, and potassium have received the most attention. Relative to group II and III metal alkyls, these are more ionic and, with the exception of some lithium alkyls, they have only limited solubility in the hydrocarbon solvents normally used in olefin polymerizations.

3.4.1.2 Ligands

Two types of ligands, an all-hydrocarbon alkyl or aryl (e.g., ethyl or phenyl), and a heteroatom or a radical containing a heteroatom (e.g., Cl or -OC$_6$H$_5$) have the potential of undergoing exchange reactions with the ligands of the transition metal. When the alkyl or aryl group is exchanged , a transition metal-carbon bond is formed as the active center. Should the heteroatom be exchanged for a ligand of the transition metal, an active center is not formed because the transition metal-heteroatom bond is not active. However, the electronic and steric environment of the metal atom is altered. If this metal atom later becomes alkylated, then this center will probably show a different stereoregulating ability relative to the other centers not bearing the heteroatom.

In addition, the change in catalyst behavior is due to the changes in size of alkyl group in metal alkyl. The preferred metal alkyls possess ethyl and isobutyl ligands. Typical examples are AlEt$_3$, Al-i-Bu$_3$, AlEt$_2$Cl, Al-(i-Bu)$_2$Cl, AlEtCl$_2$, ZnEt$_2$, BeEt$_2$, and CdEt$_2$, and all of these have been available commercially in large volume or in experimental amounts.

3.4.2 Transition Metal Salts

Relative to the metal alkyl, this component of the catalyst has been more extensively examined. In fact, in the case of titanium trichlorides, their synthesis and use in polymerization has become so specialized that they are described separately. While individual factors such as choice of metal, ligand, valence, mode of reaction, etc., are very important, it is ultimately the combined effect of these factors that decides the contribution of the transition metal salt. This was already recognized by 1957 in Natta's school, as shown in Table 3.6.

Table 3.6 Effect of Transition Metal Compound (with $AlEt_3$) on
Yield of Crystalline Polypropylene

Compound	% Crystalline polymer	Compound	% Crystalline polymer
$TiCl_2$	80-90	$TiCl_4$	48
$\alpha TiCl_3$	85	$TiBr_4$	42
$\beta TiCl_3$	40-50	TiI_4	46
$TiBr_3$	44	$Ti(OR)_4, Ti(OH)_4$	trace yield
TiI_3	10	$ZrCl_4$	51.5
$ZrCl_2$	55	VCl_4	48
VCl_3	73	$VOCl_3$	32
$CrCl_3$	36		

3.4.2.1 Choice of Metal

Nearly all of the transition metals have formed active metal salts for one or more monomers. Yet most of the more important results have been obtained with a relatively small number of metals. The number of active metals is greatest for ethylene and diminishes for propylene and higher α-olefins.

The availability of $TiCl_4$ as an inexpensive material in the 1950's undoubtedly promoted considerable research aimed at industrial applications. It is not surprising that many papers and patents have appeared that use $TiCl_4$ or a

derivative, especially TiCl₃'s and TiCl₂'s of varying compositions and crystal structures. As a result, many interesting and important findings developed with these TiCl₃'s , and this lead to more research on elucidation of mechanism, etc. The same was true for aluminum alkyls.

Other transition metals, such as Sc, V, Cr, Nb, Zr , and W have been examined. Vanadium salts attracted much attention because they predominantly led to random alternating copolymers, in contrast to blocky polymers obtained with titanium salts.

3.4.2.2 Ligands

Active catalysts for ethylene, propylene, and higher α-olefin have been made from transition metals bearing ligands of varied structures. These ligands include the groupings shown below.

From a practical point of view, not all of these are always attractive. One must select each transition metal salt on the basis of the monomer polymerized, as well as such other constraints as yields, stereoregularity. copolymer composition, morphology, or a combination of these.

Table 3.7 Ligands in Transition Metal Salts

Ligands
Cl, Br, I or F
OR (R = alkyl such as Bu, Me)
SR (R = alkyl such as Bu, Me)
NR_2 (R = alkyl such as Bu, Me)
acetylacetonate
nitroso
phosphate
chromate
π-C_5H_5-Cp
indenyl
arenes
O-C-CH_3
O
oxide
sulfide (disulfide)
sulfate
carbon monoxide

Thus, the following ground rules are suggested for the selection of a proper transition metal salt.

(a) Because it is the most active olefin and is not hampered by stereochemical limitations, ethylene can be polymerized to highly linear products with catalysts containing the largest array of transition metal salts, that is, those having different ligand structures. Economics and the balance of properties shown by the polyethylene probably dictate the choice of the salt. The variation in ligand structure is great, including sulfides, oxides, oxychlorides, dialkylamine, alkoxy, arene, acetylacetonate, cyclopentadienyl, halide (= Cl, Br, I, or F), phosphate, sulfate, and so on. Because in many of these catalysts the transition metal salt and the metal alkyl undergo exchange of ligands in varying degrees, the activity of the catalysis is sensitive to the molecular ratio of the two components. In addition, the ligand structure of the active center may be significantly different from that of the starting salt, and only little insight is gained by consideration of the structure of the parent salt. One should be wary about comparisons of activities of the transition metal salts bearing different ligands if the polymerizations are not done under similar conditions.
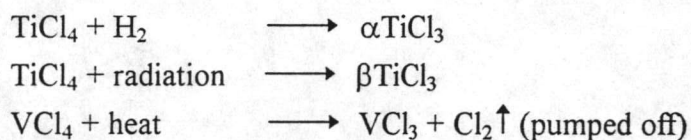
(b) Propylene is less active by an order of magnitude and higher than ethylene, and it can be polymerized to either isotactic or syndiotactic structures. For synthesis of isotactic structures, the preferred ligand is chlorine, especially in combination with Ti, V, Cr, or Nb as in $TiCl_3$, VCl_3, $CrCl_3$, and $NbCl_5$. Aluminum alkyls that have the AlE_2X or AlR_3 structures are preferred. Syndiotactic polypropylene of high crystallinity has been prepared only with vanadium salts and here the ligands can be different so long as the salt remains soluble for example, VCl_4, $VOCl_3$, $VO(OEt)_3$. Only aluminum alkyls having a structure AlR_2Cl can be used as cocatalysts. The catalyst remains soluble during the polymerization.

The choice of ligand in the copolymerization of ethylene and propylene closely follows the choice for polymerization of propylene to isotactic polypropylene if blocky copolymers are sought; the choice of ligand also follows the choice for syndiotactic polypropylene if random of prevalently alternating copolymers are sought. In the latter case, AlR_3 and $AlRCl_2$ alkyls have also been used in addition to AlR_2Cl. While the syndiotactic polymerization is done below $-50\,^\circ C$, copolymerizations are carried out above $0\,^\circ C$. An important role of the ligand in the copolymerization is to help form heterogeneous catalysts for blocky

copolymerizations or homogeneous (colloidal) catalysts if random alternating copolymerizations are sought.

3.4.2.3 Elemental Composition

The transition metal salt can have a neat composition if its synthesis did not use other metals or metal compounds.

$$TiCl_4 + H_2 \longrightarrow \alpha TiCl_3$$
$$TiCl_4 + radiation \longrightarrow \beta TiCl_3$$
$$VCl_4 + heat \longrightarrow VCl_3 + Cl_2 \uparrow \text{ (pumped off)}$$

However, a number of important titanium and vanadium transition metal salts have been prepared by reduction of $TiCl_4$ or VCl_4 with metal alkyl ($AlEt_3$, Al-i-Bu_3, $AlEt_2Cl$, or $AlEtCl_2$ and related compounds) or with metals and mixtures of metals and metal chlorides (Al or $AlCl_3$-Al mixtures). Sometime these catalysts were prepared in the polymerization reactor, often in the presence of the olefin being polymerized. Much work also has been devoted to isolating these salts and identifying their compositions. Indeed, it was found that they were contaminated with aluminum compounds, especially $AlCl_3$. In many cases, chemisorbed aluminum alkyls were probably also present when the reduction was done with an aluminum alkyl.

3.4.3 Fundamental Properties

Both the metal alkyl and the transition metal salt components play important roles in the generation of active centers. Correlation of the fundamental properties of each component to the catalytic behavior is necessary to be mentioned.

3.4.3.1 Diameter for metal in metal alkyl

Natta suggested that the most stereoregulating catalysts were those in which the metal of the metal alkyl component had a very large diameter.

3.4.3.2 Complexing ability of metal alkyl

The chemistry of the aluminum alkyl has been used to explain not only catalyst formation but also its use in polymerization. But caution must be used in reaching dogmatic conclusions. For example, we might be tempted to conclude that facile ligand exchange reactions between the metal alkyl molecules and their ability to form electron-deficient bridge complexes are related. But zinc and cadmium, unlike aluminum alkyls, undergo fast exchange reactions even though they do not form strong bridged dimers. All of these metal alkyls form active catalysts. Thus, site formation can not be directly associated with the ability of metal alkyl to form electron deficient structures. Hoeg's suggestion that four-center transition states rather than distinct intermediates may actually be involved in ligand exchange is a reasonable explanation [1].

3.4.3.3 Ionic nature of catalyst

Bushick and Stearns[56] found that the rate of polymerization correlated well with measured electrical conductivities of catalyst components. Their data supported the view that Ziegler-Natta catalysts are highly ionic in nature and that the active centers that are responsible for polymerization have ionic character. Figure 3.3 shows the dependence of polymerization of propylene on equivalent conductivity for catalysts formed by combining $TiCl_3$ and $AlEtCl_2$, $AlEt_2Cl$, or $AlEt_3$. A dependence on conductance was also found for catalysts formed by combining $Al-i-Bu_2Cl$ and $VO(OEt)_3$, $VO(OEt)Cl_2$, or $VO(OEt)_2Cl$ when these were used to copolymerize ethylene and propylene. Similarly, when ethylene was polymerized with $Al_2Et_3Cl_3-TiCl_4$ catalyst solvents containing varying amounts of benzene and heptane, rate increased about fourfold on going from pure heptane to pure benzene.
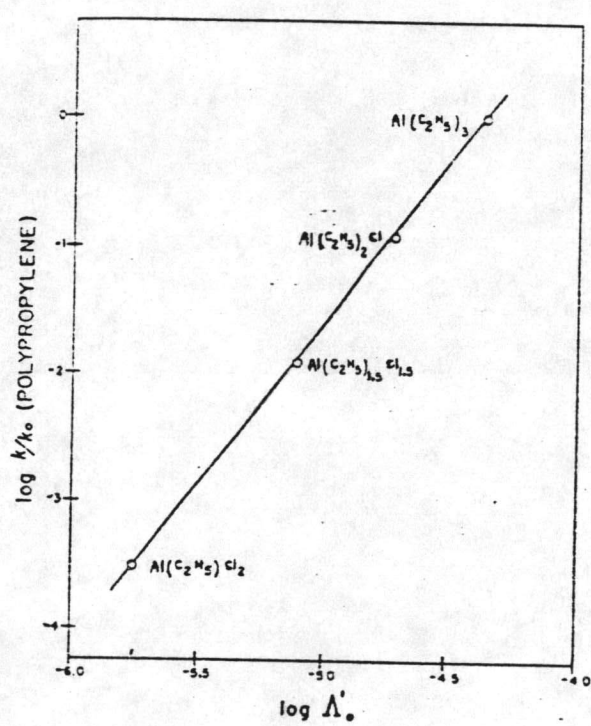
Figure 3.3 Relative rate of propylene polymerization as a function of equivalent conductivity at Λ'_0 [57].

3.4.3.4 Reducing ability of metal alkyl

It is generally recognized that metal alkyls have different abilities to reduce transition metal salts in a higher valence state. It is believed that reduction occurs via alkylated transition metal species, and since the latter can be active centers, higher catalyst activities should perhaps result with metal alkyls that have greater reducing power. Zambelli and co-workers [58] examined the polymerization of propylene with mixtures of VCl_3 and a variety of different metal alkyls, but they found no direct correlation of catalyst activity with metal alkyl reducing power.

3.4.3.5 First ionization potential of transition metals.

Natta and co-workers [59] characterized the most active salts as those having a metal whose first ionization potential lies below 7 eV and whose work function was less than 4 eV (<1.7 values in Pauling's electronegativity scale). for example, Ti, V, Cr, and Zr (Table 3.8).

Table 3.8 Dependence on Work Function and Ionization Potential

Property	Ti[a]	V[a]	Cr[a]	Mn	Fe	Ni	Zr	Mo	W
First ionization potential (eV)	6.8	6.7	6.7	7.4	7.8	7.6	6.9	7.1	7.9
Work function (in eV)	3.9	3.8	3.7	3.8	4.7	5.0	3.7	4.1	4.5

[a] Metals which form the most active salts.

In general, this proposal has been substantiated for olefins, but it is not applicable to diene polymerizations. Nickel and cobalt catalysts are highly active for butadiene.

3.4.3.6 Number of d electrons and energies of metal and olefin orbitals

In his molecular orbital (MO) treatment of the propagation step, Cossee suggested that transition metal salts containing zero to three d electrons should be most active. This has generally been found true for olefin polymerizations. Catalysts made from transition metal salts that have four or more d electrons were about 10^{-3} to 10^{-5} as active[60]. In combination with $AlEt_2Cl$, the following order of activity was found : $CrCl_2 > FeX_2$ (X= Cl, Br, or acac) $> MnX_2$ (X= Cl or acac). These divalent salts contain four, six, and five d electrons. respectively. Cossee concluded from his MO calculations that a metal center was active if the energies of the metal and olefin orbitals were approximately similar. The influence of ligands in transition metal salts was seen to alter the relative energy of the metal orbitals and, in this way, affect the activity of the metal center.

3.5 COMPLETION OF PROPYLENE POLYMERIZATION

More likely mechanisms are those in which propagation occurs at a metal-alkyl bond. This could be the transition metal alkyl, the metal alkyl activator, or an alkyl group which is bridging between these two. Despite the differences between radically produced polymers and those made using Ziegler-Natta catalysts. the radical and anionic mechanisms described briefly above are perhaps sufficiently different from conventional radical and anionic systems for the normal tests not to be appropriate. However, there are several pieces of experimental evidence which point to the active center being a metal-alkyl bond[48-50].

3.5.1 Mechanism of Propagation Site Formation

The Ziegler-Natta catalyst systems for the stereoregular polymerization of α-olefins generally contain a crystalline solid phase which consists essentially of a transition metal halide. The physicochemical condition at the surface of these crystals undoubtedly plays a major role in governing stereospecificity. Various mechanisms have been proposed to describe the surface condition. Several basic idea have been brought forth.

The proposed mechanisms are classified according to the structure of the growth center [1] :
  (1) the center is a transition metal-carbon bond,
  (2) the center is a base metal-carbon bond,
  (3) the center is a bound radical , and
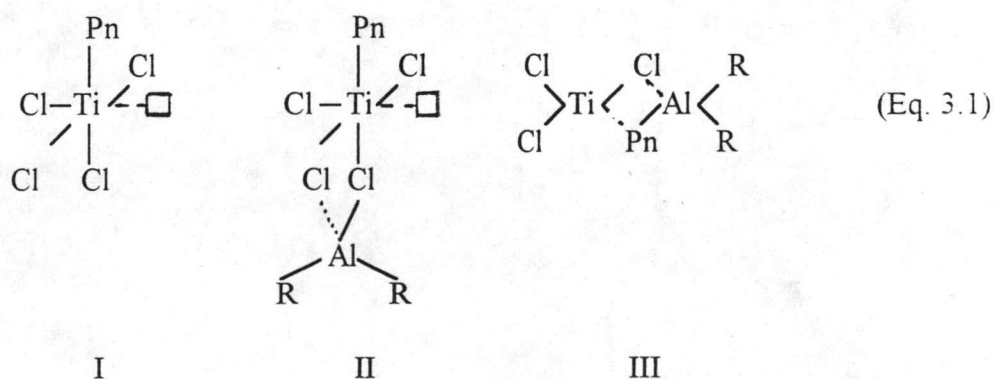 (4) the center is a bound anion.

The literature uses the terminology "monometallic" and " bimetallic" in describing both mechanisms and catalysts. When talking about mechanisms, the notations monometallic and bimetallic have been used to show that one or two metal atoms are involved (and are essential) in the growth step, respectively. On the other hand, some workers refer to metal alkyl-free catalysts and Ziegler-Natta catalysts as monometallic- and bimetallic-coordination anionic catalysts, respectively.

Natta and co-workers judiciously avoided this problem by using the simple designation Me-C (or M-C or cat-E) for the active center without requiring M to be the base metal or the transition metal [5].

Natta and co-workers accepted the scheme (b) as applicable to isotactic polymerizations and used it advantageously in kinetic treatments.

This mono and bimetallic nomeclature can get cumbersome for certain mechanistic proposals. Consider, for example, three types of active centers that have been proposed for the active metal-carbon bond M-Pn (Pn is the growing polymer chain, M is Ti or Al, and Cl is chlorine ligands of $TiCl_3$ crystal surface or attached to Al) (see structures I, II, and III in (3.1)). A common feature of growth at all three structures is the complexing of olefin at the Ti center. In structures I and II, however, growth takes place in the Ti-Pn bond, while in structures III, the Al-Pn is the growth bond. According to some authors, the presence of AlR_3 as part of the complex is essential for a number of reasons : (1) it stabilizes the transition metal-carbon bond and prevents its decomposition, (2) it makes the transition metal- carbon bond more active for polymerization, and/or (3) it is necessary to orient the complexed α-olefin in the isotactic configuration.

$$
\text{(Eq. 3.1)}
$$

Structure I, II, III (Eq. 3.1)

I   II   III

Surface of Catalyst

An-----ĊH-CH₂-P
R

ĊH------- CH₂
R

An-----ĊH-CH₂-CH-CH₂-P
R

An-----H + CH=CH-CH-CH₂-P

(a)

Surface of Catalyst

Me----CH₂-ĊH-P
R

CH₂------- ĊH
R

Me-----CH₂-ĊH-CH₂-ĊH-P
R   R

Me-----H + CH₂=Ċ-CH₂-ĊH-P
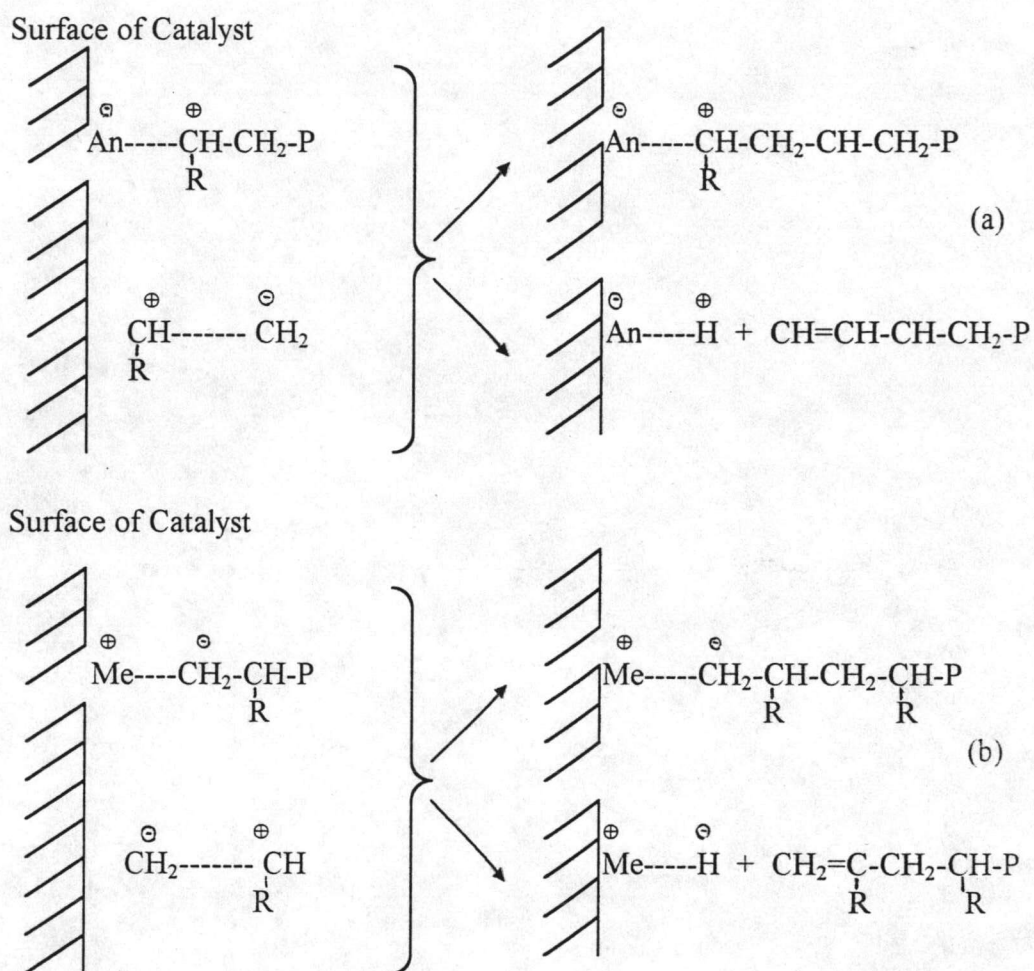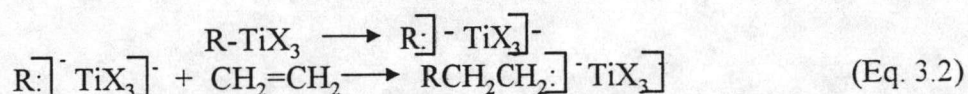R   R

(b)

Figure 3.4 Scheme of polymerization of vinyl monomers under formation of isotactic polymer[65].
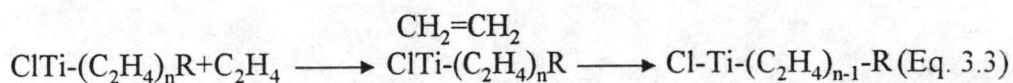
3.5.2 Proposed Mechanisms

The proposed mechanistic schemes are presented here in four classification that serving a worth-while purpose in advancing Ziegler-Natta chemistry. They deserve some attention even though most are now outdated.

3.5.1. Propagation at a transition metal-carbon bond

There are again numerous mechanism, this time proposing that polymerization occurs at the transition metal alkyl. Various valencies have been suggested for the titanium, ranging from four to two. An early suggestion was that polymerization occured at a tetravalent alkyltitanium halide [46], as shown below.

$$R-TiX_3 \longrightarrow R{:}]^- \, TiX_3]^-$$
$$R{:}]^- \, TiX_3]^- + CH_2{=}CH_2 \longrightarrow RCH_2CH_2{:}]^- \, TiX_3] \qquad \text{(Eq. 3.2)}$$

Another mechanism employing a titanium in a lower valence state, such as RTiCl, was suggested in 1958 by Ludlum and co-worders [60] to be the active site. It was proposed that an alkyltitanium chloride with a valence of II complesed with an ethylene molecule, which then wasd inserted into the titanium-carbon bond, as shown in Eq. 3.3.
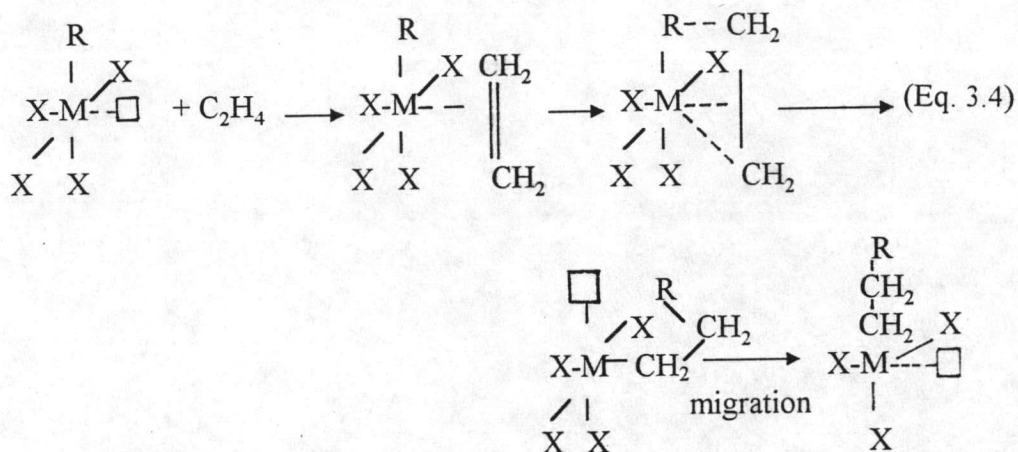
$$ClTi{-}(C_2H_4)_nR + C_2H_4 \xrightarrow{\;CH_2{=}CH_2\;} ClTi{-}(C_2H_4)_nR \longrightarrow Cl{-}Ti{-}(C_2H_4)_{n-1}{-}R \;\text{(Eq. 3.3)}$$

These workers reported that the rate of polymerization of ethylene with $AlEt_3$-$TiCl_4$ (or Al-i-Bu_3-$TiCl_4$) catalyst was maximum when the average valence state of titanium was II.

Probably the most generally accepted and the most comprehensive mechanism for olefin polymerization is that of Cossee. He proposed that the active site was a transiition metal atom in an octahedral configuration and that one position was vacant, $\square$, due to a missing ligand, the remaining position being occupied by one alkyl and four ligands [61]. In structure shown below, M is the transition metal ion, R is the alkyl derived from metal alkyl or growing polymer chain, X is the ligands of crystal (Cl in $TiCl_3$) and $\square$ is the vacant octahedral position.

$$
\begin{array}{c}
R \\
| \;/\; X_2 \\
X_4 - M - \square \\
/ \quad | \\
X_1 \quad X_3
\end{array}
$$
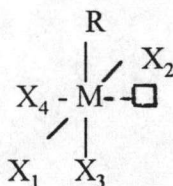
One growth step in Cossee's mechanism is shown here, as R is the growing polymer chain and $\square$ is the vacant octahedral position.

```
  R                    R                   R--CH₂
  |  X                 |  X  CH₂            |  X
X-M--□  + C₂H₄ ──→  X-M-- --  ‖    ──→   X-M---  |     ──────→ (Eq. 3.4)
 / |                / |     ‖             / |   `·
X  X               X  X    CH₂           X  X   `CH₂
```

```
        □       R                  R
        T  /X  \  CH₂              CH₂
      X-M─ CH₂         ──────→    CH₂  X
       / |         migration     X-M---□
      X  X                         |
                                   X
```

Repetition of this growth step is responsible for the polymerization of the olefin to a high molecular weight polymer. In Cossee's scheme, the growing alkyl group and the vacancy exchange octahedral positions after each insertion of monomer, and the R group must migrate back to its former position. Cossee also suggested a driving force for the polymerization on the basis of molecular orbital calculations [61-62]. The olefin is coordinated to the transition metal ion at the vacant octahedral position through π bonding. Figure 3.5 shows a schematic picture of the spatial arrangement of the relevant orbitals in this π bond.

Figure 3.5 describes the π complex in terms of a molecular orbital diagram, where M is titanium in the heterogeneous catalyst containing $TiCl_3$. ϕ_{RM} is the energy level of the alkyl titanium bond. This bond apparently stable when $RTiCl_4$ is not complexed with an olefin because the catralyst can be stored for a long time. ΔE represents the energy that an electron in the Ti-R bond must be excited to in order to weaken the bond. ΔE is large enough barrier to maintain the Ti-E bond intact in the absence of olefin.

When an olefin molecule is coordinated to the $RTiCl_4$ octahedral complex, however, a new energy level $\psi_2(d_{yz})$ is formed by mixing metal d orbitals and ethylene antibonding orbitals. This new orbital is sufficiently from the metal-carbon bond ψ_{RM} can be easily excited into it. If   is smaller than the critical energy gap in the Chatt and Shaw model, the alkyl process to the nearest carbon atom of the olefin while, at the same time, the other side of the olefin connects itself to the metal. (3.4) shows this reaction path.
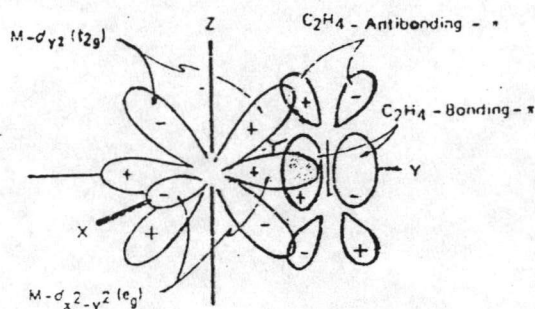
Figure 3.5 Schematic picture showing spatial arrengment of the relevant orbitals in a" π bond " between a transition metal and C_2H_4.
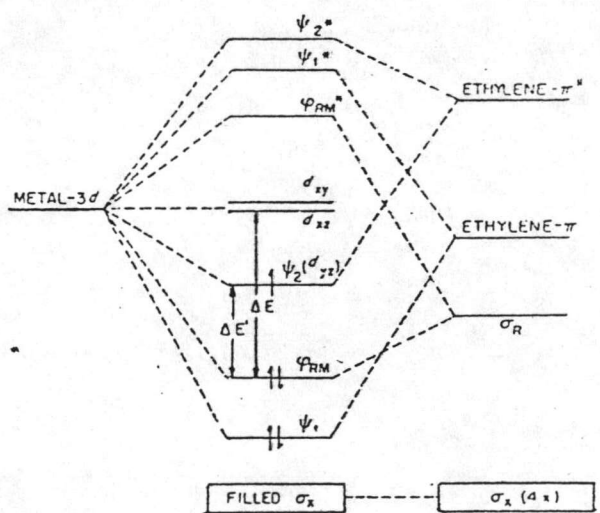

Figure 3.6 Tentative molecular orbital energy diagram for the octahedral complex $RTiCl_4$.

This mixing of orbitals results in lowering the activation energy for the rearrangement in which the alkyl group moves from the transition metal toward the nearest carbon atom of the olefin. In order for the isolated transition metal-carbon bonds to be stable in the absence of coordinated olefin, the electronegativity of the metal ion must be sufficiently low. The metal-carbon bond, however, must be sufficiently destabilized when an olefin becomes coordinated in the vacant position.
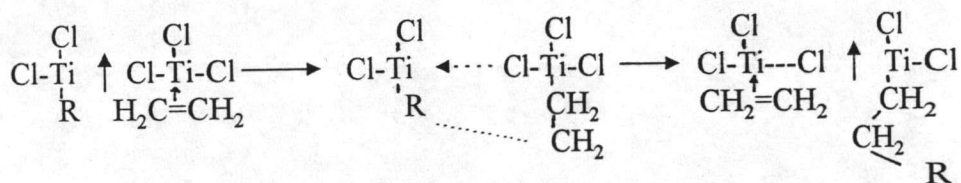
Cossee's model predicts that only certain transition metals will be highly active as catalysts. According to his molecular orbital energy diagram, the catalyst activity of the transition metal compound does not depend on the presence of electrons in the d_{yz}, d_{xz}, and d_{zy} orbitals. No two electrons, however, are allowed to be present in the ψ_2 (d_{yz}) orbital; this means that transition metal ions having one to three unpaired electrons are most effective . The specific action of the transition metal is most favorable only when the energy of the metal 3d level is between the bonding and antibonding levels of the olefin. A modification was made in 1966 in which Cossee described nuclear motions (vibrations) and subsequently the electron configurations and the energy of the system as a function of the positions of the nuclei [62]. However, similar conclusions were reached.

Begley and Pennella [63] calculated the electronic energy levels for the molecular orbital of the octahedral center $TiCl_4$ and the corresponding olefin complex, $RTiCl_4$ olefin. They considered an electronic transition from the highest filled orbital to the half-filled orbital above to be the initial step in the olefin insertion reaction (the growth strp). The energy of this transition was calculated to be about 10 to 14 kcal/mole, corresponding to the most widely found value for Ziegler-Natta polymerizations. They suggested, then, that this electronic transition is actually the controlling step in the reaction. Barriers of 3.02, 1.07, and 0.7 eV were calculated for excitation of electrons from the highest filled orbital to the lowest empty or partly filled orbital when the Ti-C was present in the structures CH_3TiCl_3 (an isolated molecule), to $RTiCl_4$, and in $RTiCl_4$.olefin complex, respectively. The latter two are Ti centers in the crystal lattice of the heterogeneous catalyst. Begley and Pennella agreed with Cossee that insertion of the olefin molecule into the Ti-C bond could occur only if the Ti-C bond was weakened by complexing the $RTiCl_4$ center with the olefin. According to their calculations, the energy barrier was reduced from 1.07 to 0.7 eV.

In all of the above mechanisms, the center involves only one transition metal atom. Several mechanisms have been proposed in which propagation took place at a Ti-C bond, but which involved an active participation of neighboring Ti or Al atoms.
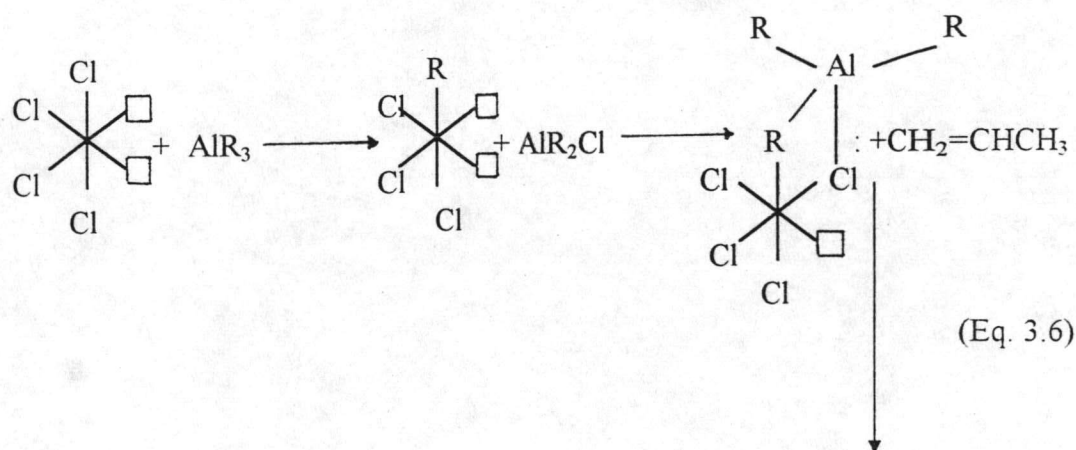
A mechanism was proposed by De Brujin [64] in which the olefin coordinated at one titanium but is interposed into a metal-carbon bond of another titanium atom, as shown in (3.5). The growing alkyl migrated between two adjacent titaniums on the surface of the $TiCl_3$ crystal surface.
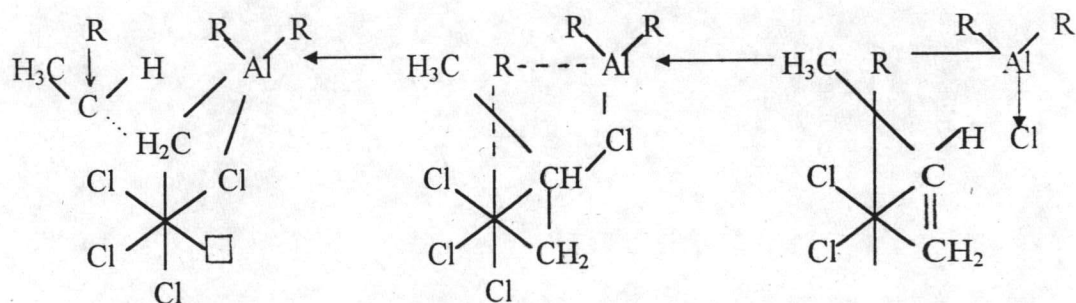
$$\begin{array}{ccc} \text{Cl} & \text{Cl} \\ \text{Cl-Ti} \uparrow \text{Cl-Ti-Cl} \\ \text{R} \quad \text{H}_2\text{C}{=}\text{CH}_2 \end{array} \longrightarrow \begin{array}{c} \text{Cl} \quad\quad \text{Cl} \\ \text{Cl-Ti} \longleftarrow \text{Cl-Ti-Cl} \\ \text{R} \quad\quad \text{CH}_2 \\ \text{CH}_2 \end{array} \longrightarrow \begin{array}{cc} \text{Cl} & \text{Cl} \\ \text{Cl-Ti---Cl} \uparrow \text{Ti-Cl} \\ \text{CH}_2{=}\text{CH}_2 \quad \text{CH}_2 \\ \text{CH}_2 \\ \text{R} \end{array}$$
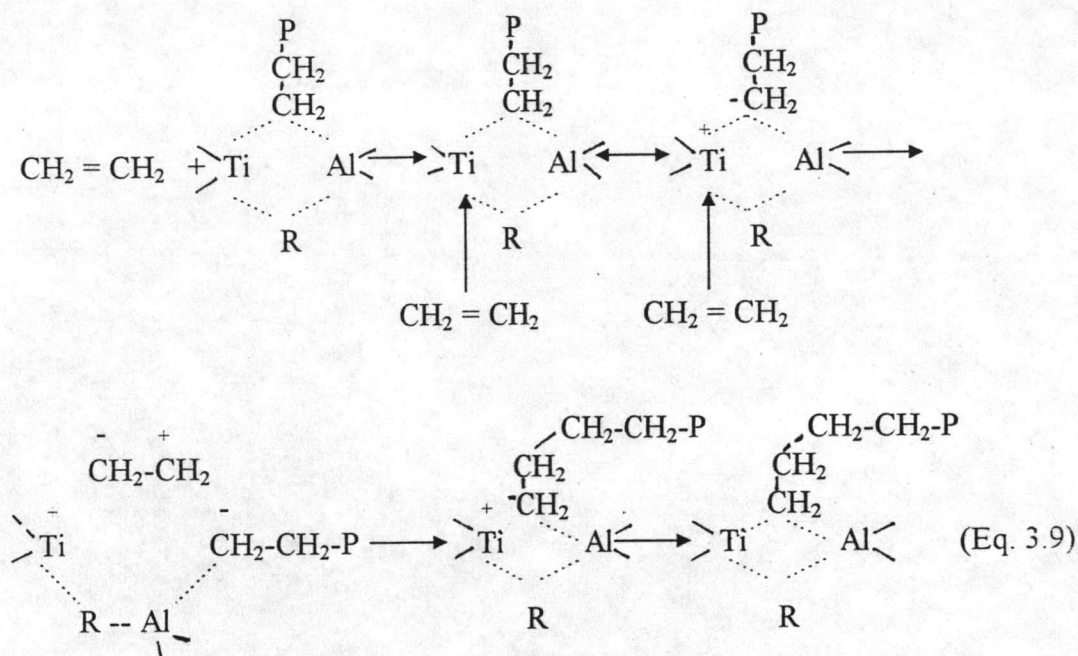
<div align="right">(Eq. 3.5)</div>

Rodriguez and van Looy [65] require a complexed aluminum alkyl as an integral part of the center, even though growth takes place at a transition metal-carbon bond, as shown in (3.6), where•denotes Ti and □ denotes a chlorine vacancy. This mechanism has features of the Cossee model, as well as of earlier bimetallic models proposed by Nattta and co-workers, and Patat and Sinn. Steric interactions between the metal alkyl and the complexed α-olefin are said to be responsible for stereochemical control.

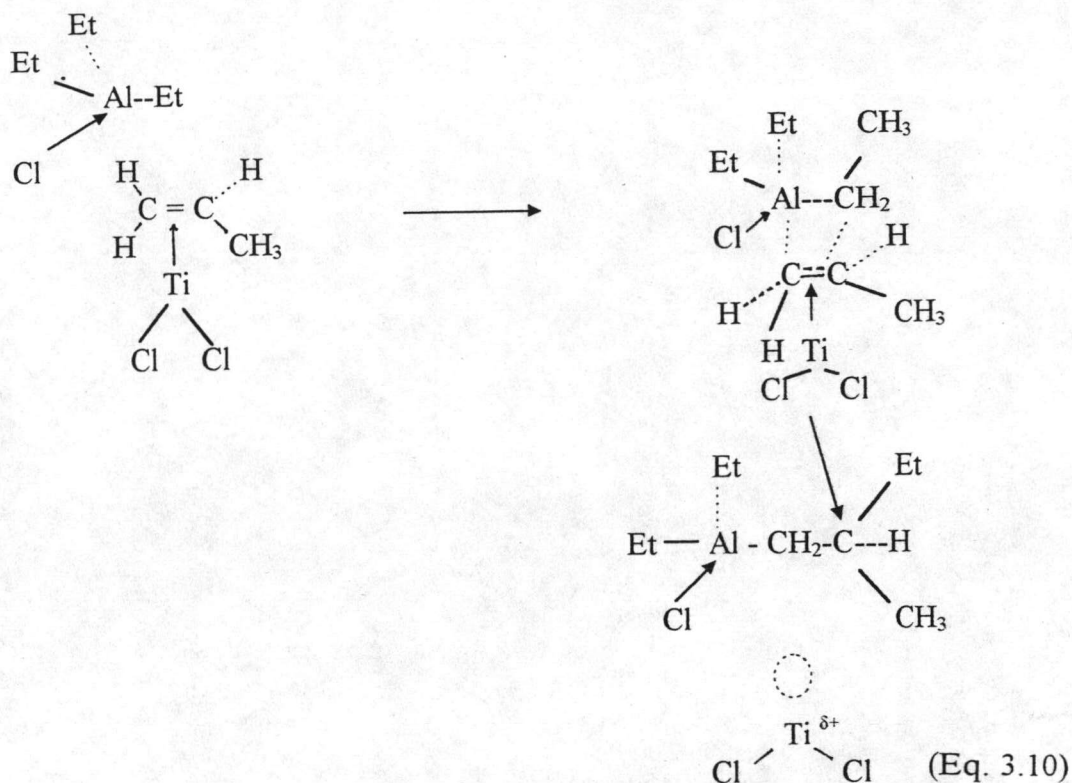<div align="right">(Eq. 3.6)</div>

3.5.2 Propagation at a base metal-carbon bond

In the early days of Ziegler-Natta history, most workers believed the growth center to be the base metal-carbon bond, that is, the Al-C bond in the catalyst $AlEt_3$-$TiCl_3$. Of these mechanisms, those proposed in 1960 by Natta and in 1958 by Patat and Sinn contain the most cogent features.

$$\overset{\underset{\displaystyle}{}}{>}Ti \cdots\cdots\overset{X}{}\cdots\cdots Al< \qquad (Eq.\ 3.7)$$
$$Pn$$

The structure shown above (where Pn is the growing polymer chain and X is halogen) is common to both bimetallic mechanisms. The monomer is coordinated to the titanium while the Ti-polymer partial bond is simultaneously broken.

In the Natta mechanism [18], the olefin becomes polarized and inserted into the aluminum-carbon bond.

$$(Eq.\ 3.8)$$

In the Patat-Sinn mechanism [54], the olefin becomes partially bonded between the methylene of the last added monomer unit and the titanium atom. The latter is partially bonded via an alkyl bridge to the aluminum. When a bond forms between the olefin and the methylene, the methylene unit becomes detached from the aluminum and now the new methylene unit becomes partially bonded to both metal atoms.

$$
CH_2=CH_2 + \overset{P}{\underset{R}{\underset{\displaystyle |}{\overset{\displaystyle CH_2}{\overset{|}{\underset{\displaystyle CH_2}{}}}}}} Ti \quad Al \longleftrightarrow \quad Ti \quad Al \longleftrightarrow \quad \overset{+}{Ti} \quad Al \longrightarrow
$$

(Eq. 3.9)

Other mechanistic schemes were proposed in with the Al-C was stated to be the growth center. These are mentioned briefly here, emphasizing only the silient feature of each proposal.

Eirich and Mark [55] also proposed a similar mechanism, which employed adsorbed layers of alkylaluminum chloride on the titanium chloride crystals.

An ion pair complex of $TiCl_4$ and $AlEt_2Cl$ was investigated by Uelzmann[56] to propose the AlR_3Cl anion as the growth center and the cation $TiCl_2$ as olefin polarizing site.

Boor[57] proposed a concerted mechanism as shown below, in which nond breaking and making occured simultaneously.

Et

Et ⋰

Al--Et

Cl

    H   H

    C = C

  H | CH_3

    Ti

  Cl   Cl

⟶

    Et CH_3

Et

  Al---CH_2

Cl   H

   C=C

 H CH_3

  H Ti

  Cl Cl

  Et   Et

Et — Al - CH_2-C---H

  Cl CH_3

$Ti^{\delta+}$

Cl   Cl   (Eq. 3.10)

Bier [58] and Gumboldt and Schmidt [59] proposed that aluminum alkyls are adsorbed onn the $TiCl_3$ surface in two ways, as shown below.

$$\begin{bmatrix} Cl & & R \\ Cl\text{-}Ti & & Cl\text{-}Al\text{-}R \\ Cl & & R \end{bmatrix}^{+\quad -} \quad \text{and} \quad \begin{matrix} Cl & R \\ Cl\text{-}Ti & * & Al\text{-}R \\ Cl & R \end{matrix} \qquad (Eq.\ 3.11)$$
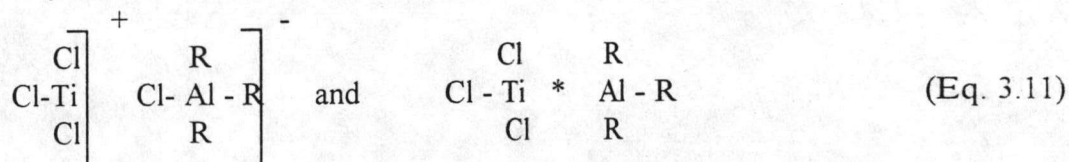
During the growth step, the growing polymer chain migrates from one aluminum atom and becomes attached to the olefin that is coordinated to an adjacent aluminum alkyl. A simultaneous electron transfer occurs between adjacent titanium atoms. The $TiCl_3$ surface acts to activate and stabilize the metal alkyl growth centers but does not coordinate the olefin itself. In a way, this mechanism can be regarded as an Aufbau reaction, which is enhanced by the $TiCl_3$ surface, as shown in Eq. 3.11.

    Cl   R   Cl   R

Cl-Ti   Cl-Al-P   Cl-Ti   Cl-Al

    Cl   R   Cl   R

    Cl   R   Cl   R

Cl-Ti   Cl-Al-CH_2-CH_2 → Cl-Ti   Cl-Al-CH_2-CH_2-P

    Cl   R   Cl   R

(Eq. 3.12)
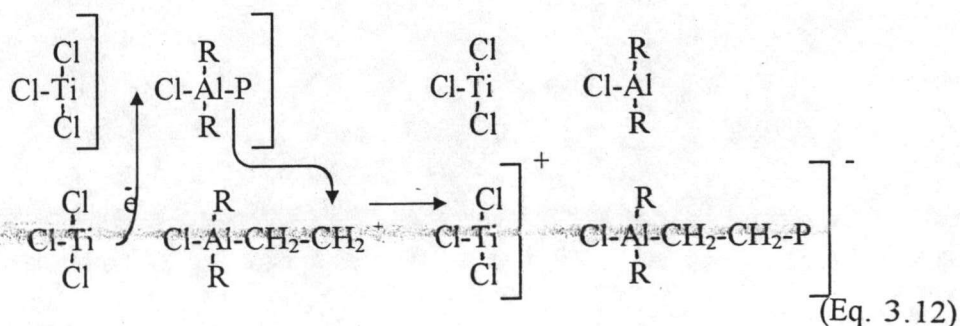
The already mentioned mechanism and mentioned else where in this view suggest that the $TiCl_3$ surface simple acts to activate adsorbed aluminium alkyl and that polymerization occurs when the polymer chain transfers from one aluminium to an olefin which is coordiated to another. Electroneutrality is maintained by electron transfers through the $TiCl_3$ surface. The view that an active site is formed when a metal alkyl is adsorbed on the surface of the transition metal salt has been exploited in kinetic treatments with the application to Langmiur-Hinshelwood and Rideal rate laws.

3.5.1. Radical mechanism

Nenitzescu and co-workers [46] suggested the possibility of a radical mechanism, shown below.

$$nR\text{-}Al + TiCl_4 \longrightarrow R_nTiCl_{4-n} + n\ AlCl\ (n \leq 4)$$

$$RTiCl_3 \longrightarrow R\cdot + TiCl_3$$

$$R\cdot + CH_2=CH_2 \longrightarrow R\text{-}CH_2CH_2 \longrightarrow polymer \qquad (Eq.\ 3.13)$$
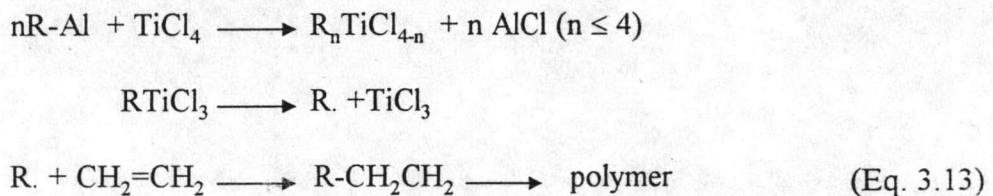
About the same time (1956), Friedlander and Oita proposed a free radical mechanism in which initiation occurred when an electron was transferred from the metal to the olefin (Figure 3.7)

Topchiev, Krentsel, and co-workers [51] proposed that initiation occured by a R. radical, which is bound to the surface of the $TiCl_3$ as shown below.

$$(Eq.\ 3.14)$$
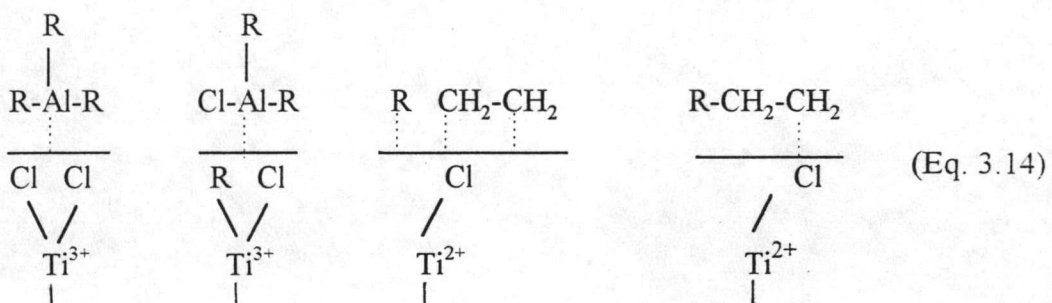
cross section
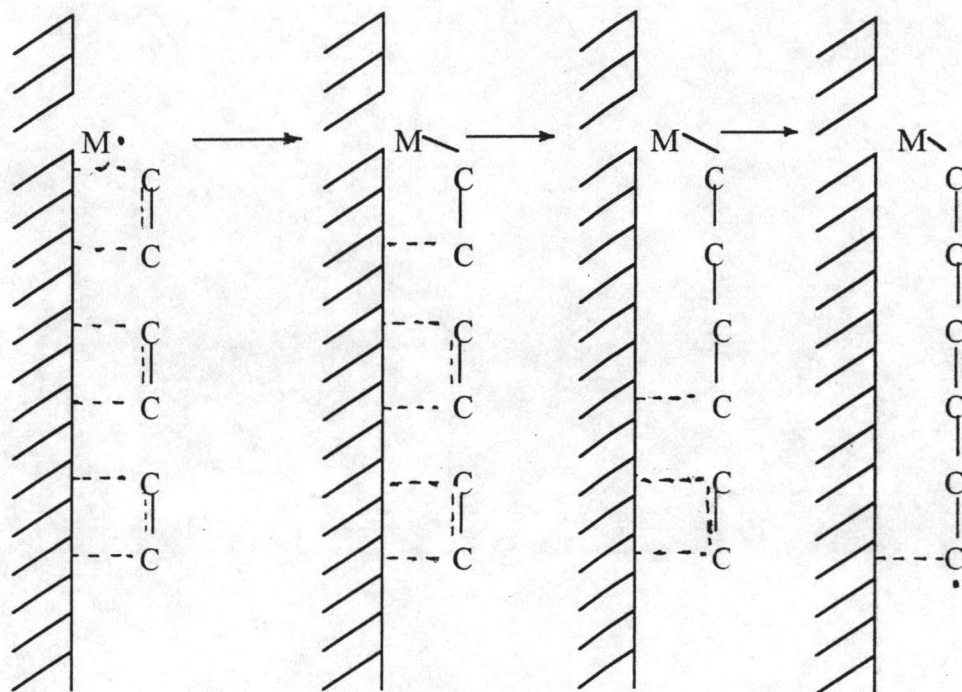
Figure 3.7 Friendlander and Oita's radical mechanism where initaiton is effected by the transfer of an electron from the transition metal to the olefin.

The chemisorbed aluminum alkyl alkylates the $TiCl_3$ surface, and the formed Ti-R decomposes to yield an R. radical that adds to ethylene to form a new radical. The new radical also remains bound to the surface and adds another chemisorbed ethylene molecule. This process is repeated with the radical being transferred to the last added monomer each time. Repetition of this step constitues the polymerization; both the radical and the reacting ethylene molecules are bound to the $TiCl_3$ surface.

The source of the radical is the aluminum in the mechanisms of Duck [52] and Van Helden, Kooyman, and coworkers [53]. In the Duck mechanism, one aluminum center is involved (Eq. 3.15).

(Eq. 3.15)
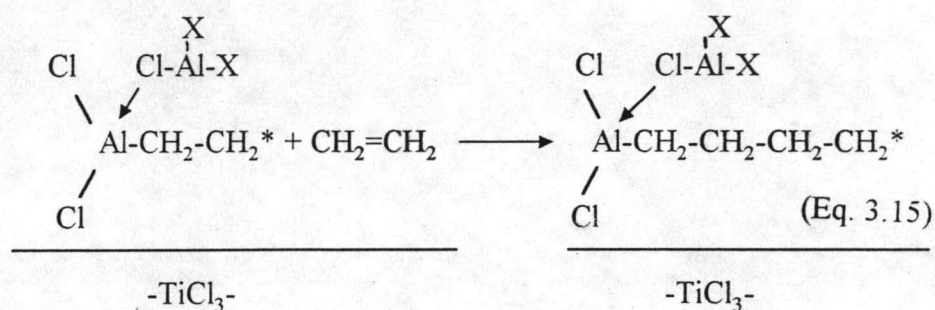
while in the Van Helden, Kooyman mechanism two aluminum atoms participate (Eq. 3.16). In both mechanisms, the $TiCl_3$ stabilizes the radical species.

(Eq. 3.16)
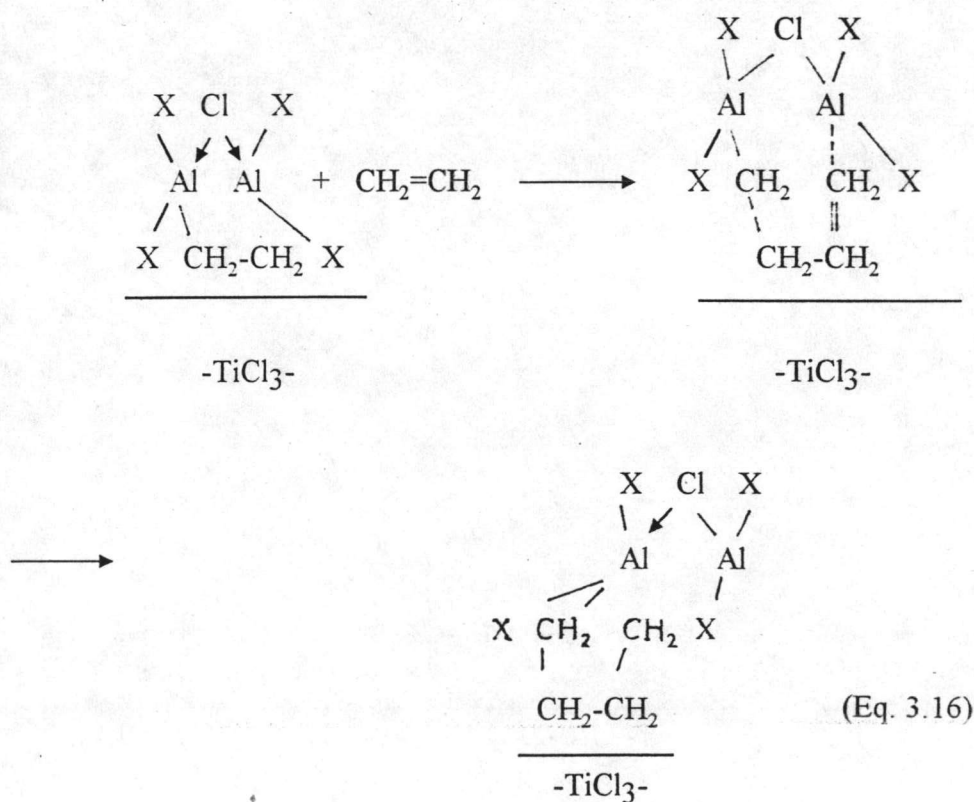
3.5.2.4 Anionic mechanism

Gilchrist [86] suggested an anionic mechanism that differs from the coordinative-anionic types in that the anionic end of the polymer chain is not fixed to a metal center (3.17). A transfer of R anion from the adsorbed metal alkyl to the adsorbed olefin initiates the polymerization. Propagation occurs because this anionic end continues to add to adsorbed olefin molecules.

$$
\begin{array}{c}
\text{Bu} \quad \text{Bu} \\
\diagdown \diagup \\
CH_2 = CH_2 \quad Zn \\
Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \\
Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti
\end{array}
$$

$$\downarrow$$

$$
\begin{array}{c}
\text{Bu} \quad\quad \text{Bu} \\
\diagup \quad\quad | \\
CH_2 = CH_2 \quad CH_2\text{-}CH_2 \quad Zn \\
Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \\
Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti
\end{array}
$$

$$\downarrow$$

$$
\begin{array}{c}
\text{Bu} \quad\quad\quad \text{Bu} \\
CH_2 \quad\quad | \\
CH_2 \quad\quad Zn \\
CH_2\text{-}CH_2 \\
Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \quad Cl \\
Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti \quad Ti
\end{array}
$$

(Eq. 3.17)
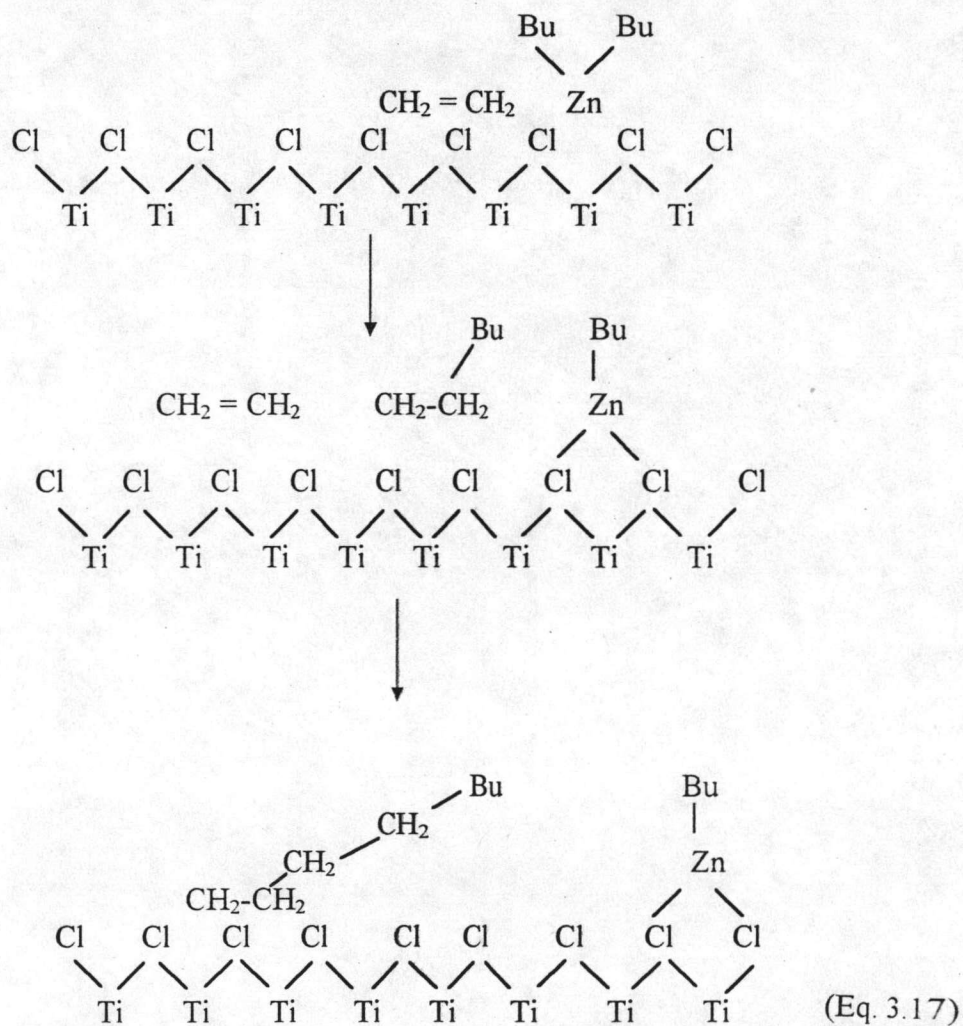
3.5.3 Mechanisms for Stereochemical Control of α-Olefins

Propylene and higher α-olefins are polymerized in the presence of heterogeneous catalysts to polymers that can have low to very high isotacticity. Only propylene, however, has been polymerized to a syndiotactic polymer, and it can also be obtained in low to very high steric purity. Soluble catalysts are most effective, but a few percent of a particlly syndiotacitc polymer have been obtained with specific heterogeneous catalyst.

The growth step involves complexing of the olefin to the transition metal followed by a cis-insertion, or more accurately, by a cis-ligand migration. It is convincingly established that propylene adds to form a primary metal alkyl (primary addition) in an isotactic propagation. Recent experimental work suggests that a secondary metal alkyl (secondary addition) is formed in a syndiotactic propagation, but this needs independent confirmation.

The driving forces for both isotactic and syndiotactic are steric in nature. The asymmetric nature of each center in the heterogeneous catalyst forces the propylene to always add either in the d or in the l configureation, and isotactic chains are formed. This driving force is absent in the soluble catalyst that polymerizes propylene at -78 °C.

In this polymerization, steric interactions between the methyl groups of the last added and the incoming polypropylene molecule to be inserted in opposite configurations after each growth step, and syndiotactic polypropylene is obtained.

3.5.3.1 Mode of Addition

This section considers the importance of complexing, cis- vs. trans-addition and primary vs. secondary addition.

3.5.3.1.1 Complexing vs. direct insertion of olefin

Most workers have taken the view that the olefin molecule forms a complex with the transition metal atom of the active center just before it is inserted into the metal-carbon bond.

Danusso and Sianesi [87] investigated the homo- and copolymerization of a series of vinyl aromatic monomers that differed in the electron density at the double bond. Figure 3.8 summarizes these results in plot of log α (relative reactivities in the homopolymerizations) and log r_2 (relative reactivities in the copolymerizations) vs. Hammet's σ values for each substituent. The monomers that had comparable steric requirements lined up on the diagra in a straight line with a negative slope. This indicated that there was a strong polar affect of the substituent on the rate of addition. Electron-donating substituents in the para-position gave higher rates. Polarization of the styrene monomers was suggested.
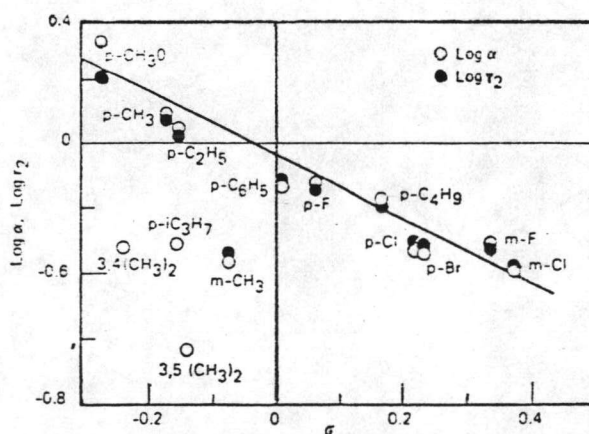
Figure 3.8 Representation on a Hammett diagram of relative reactivities in the homopolymerization, O, and the reactivity ratios r_2 in the copolymerization, ●, of a set of nuclear substituted styrenes (reference monomer is styrene).

These authors proposed that once the complex was formed, electron movement 1 preceded electron movement 2, as showing structrue I.

$$\delta^+ \qquad \delta^-$$

Ar CH-----CH$_2$

$\uparrow 2 \qquad \downarrow 1$

P CH$_2$-----Cat

I
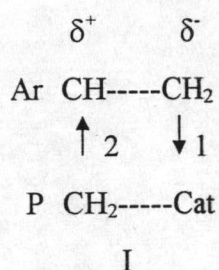
Danusso and Sianesi pointed out that reactivities of monomers incationic and anionic coordinative polymerizations increased when the electron density at the double bond increased. In conventional anionic polymerizations the reverse was true, and in this case, process 2 could precede process 1 via the path shown in structrue II, where R is an electron-attracting group.

$$\delta^+ \qquad \delta^-$$

CH$_2$-----CH-Ar

$\uparrow 1 \qquad \downarrow 2$

P CH -----Cat

R$^-$

II
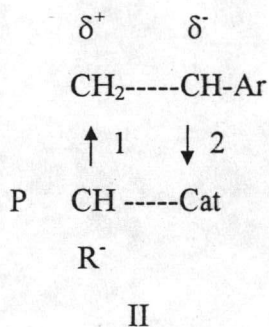
3.5.3.1.2 Primary vs secondary addition

The α-olefin can potentially add in two ways, primary addition, as shown in (3.18), or secondary addition, as in (3.19).

$$\overset{\text{CH}_3}{\underset{|}{}}$$

Ti-Pn + CH$_2$=CHCH$_3$ ⟶ Ti-CH$_2$-CH-Pn   (Eq. 3.18)

$$\text{Ti-Pn} + \text{CH}_2=\text{CH-CH}_3 \longrightarrow \overset{\overset{\textstyle CH_3}{\textstyle |}}{\text{Ti-CH-CH}_2\text{-Pn}} \qquad \text{(Eq. 3.19)}$$
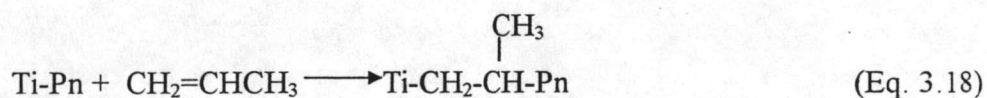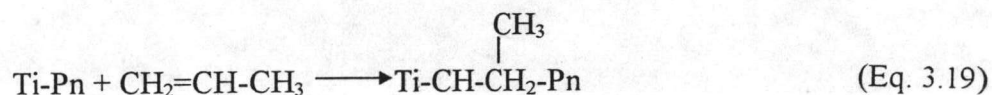
These two-modes differ in the way the α-olefin becomes inserted, that is, the unsubstituted end becomes attached to Ti in a primary addition, while in the secondary addition, it is the substituted end that becomes attached to Ti.

In 1969 and 1970, Takegamin and Suzuki [88,89] reported that, while primary addition occurred for the isotactic-specific catalysts AlEt$_3$-TiCl$_3$ and AlEt$_3$-VCl$_4$ (heterogeneous systems), secondary addition occurred when soluble, syndiotactic-specific catalysts were used such as AlEt$_2$Cl-VCl$_4$ or the same plus anisole. This conclusion was based on the insertion of one molecule of the olefin(cyclohexene, 1-pentene, or 4-methyl-1-pentene) into the V-C bond. With pentene and 4-methyl-1-pentene and AlEt$_2$Cl-VCl$_4$ catalyst, the amount of a secondary alkyl exceeded the primary alkyl by four times or more at -70°C. At higher temperatures, the primary metal alkyl resulted. The primary metal alkyl was said to have relatively lower activity at 70°C but higher activity above 0°V.

3.5.3.1.3 Cis vs Trans addition

That the addition of olefin molecules in both isotactic and syndiotactic propagations was cis was established by Natta [90], Miyazawa [91], and Zambelli [92,93] and their co-workers using deuterium-labeled propylenes. Figure 3.9 shows the expected stereochemistry of the added deuterium-labeled propylene if the addition were cis or trans. Cis-monomers gave threomonomer units while trans-monomers gave erythro units when cis- and trans-1-d-propylene were homopolymerized. This showed that the addition was cis for isotactic-specific catalysts.

3.5.3.2 Isotactic Propagation

The discovery by Natta and co-workers that some binary mixtures of metal alkyls and transition metal salts wrer able to polymerize α-olefin to isotactic polymers is just as remarkable as their ability to polymerize these olefins at all. It was also Natta who first recognized the importance of cryltal surface as the primary driving force for the isotactic propagation of α-olefin. These are presented here according to the following themes : (1) active participation of metal alkyl molecule, (2) steric reputations between the α-olefin and the ligands of the center, (3) active participation of the helix, and (4) other models.

3.5.3.2.1. Active Participation of the Metal Alkyl

Natta [94] suggested that the active centers in the isotactic-specific heterogeneous catalyst were bimetallic complexes of metal alkyl molecules and transition metal atoms that were located on the surface of the crystal. Rokiguez and Van Looy [95] agreed with Natta and proposed the path of isotactic propagation, as shown in Eq. 3.18

From their experiment data, they concluded that these titanium centers were present on lateral faces and defects. They proposed that each Ti had two missing chlorines(vacancies). Isotactic orientation was favored because the propylene molecule can complex with the exposed Ti center only in one configuration, that is, with its methyl group directed away from the alkyl groups of the aluminum atoms.
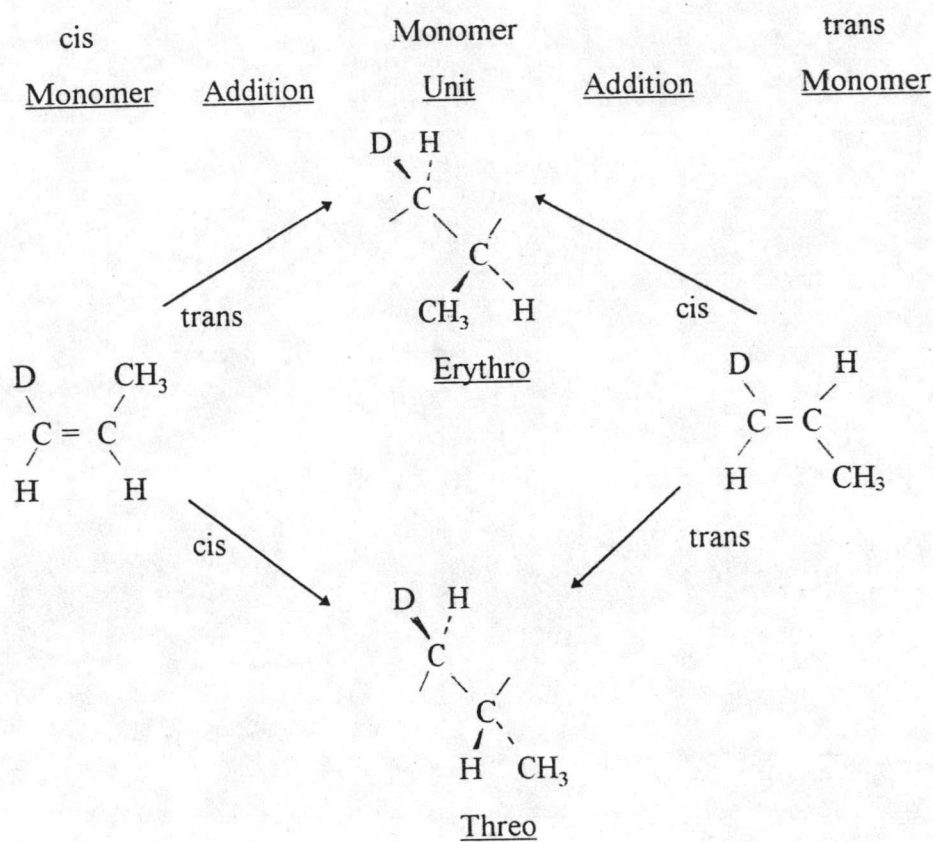
Figure 3.9   Potential stereochemical structures from cis- and trans-additions

(Eq. 3.20)
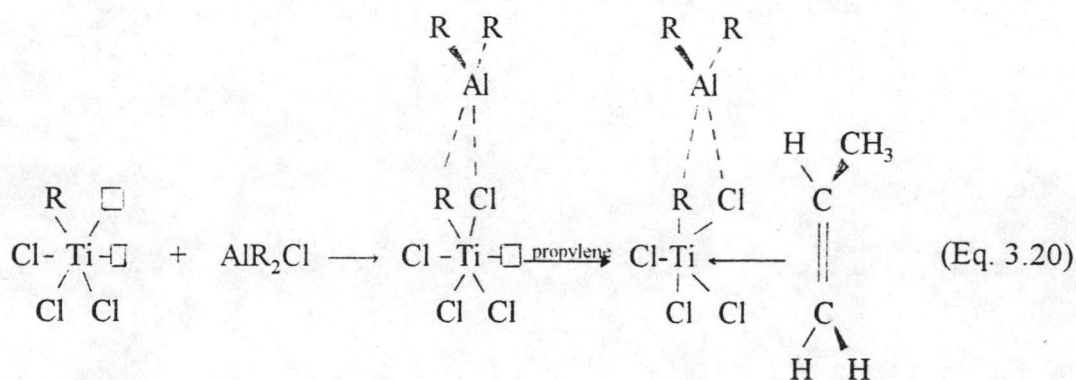
3.5.3.2.2. Steric Repulsions between the Olefin and Ligands of the Center

The basic idea of these proposals is that the prefered complexing mode minimized steric interactions between the pendent group of the α-olefin and the ligands of the active center to whicg it is complexed as well as adjacent atoms. The isotactic scheme had its beginning in the recognetion by Natta in 1955 that the isotactic propagation required an specific surface of crystalline transition metal salts.

The idea that isotactic propagation is intimately linked to the geometry of an exposed Ti (chlorine vacancy) was worked out independently for both bimetallic complexes [96] and monoalkylated titamiums [97] as active centers. The exposed Ti is an important feature of these mechanisms in two ways: (1) the olefin can complex at the vacant octahedral position and thereby its energetics become more suitable for addition, and (2) the unique ligand environment can force of favor an complexing mode corresponding to one or the other configuration.

3.5.3.2.3. Actice Participation of the Helix

Coover [99] speculated that the rate of placement preserving the symmetry of the helix was faster than the rate of the alternate placement. Thus, the driving force was due to preferntial placement of the α-olefin as a result of interactions between the α-olefin and the helix (Figure 3.10)

3.5.3.2.4. Other Models

Luisi and Mazo [100] gave developed a statistical model that would predict the formation of isotactic, atactic, syndiotactic, and stereoblock polymer in terms of the asymmetry of the active center and the interactions of the incoming monomers, as well as those added last. Since these parameters are not measurable, predictions cannot yet be made with this model.
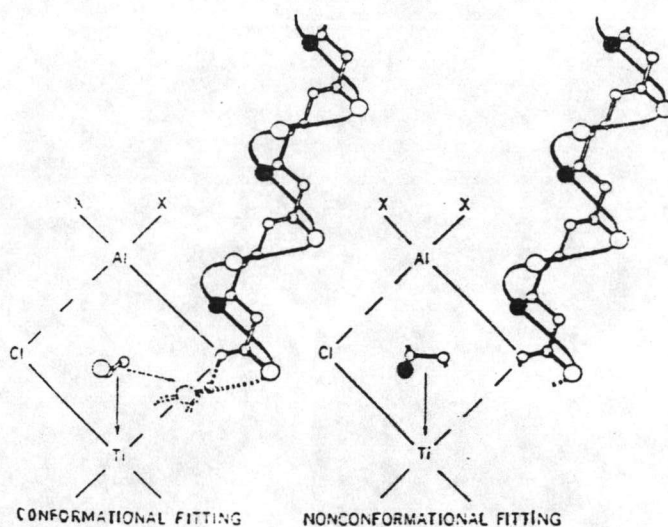
Figure 3.10 Helical model conformational fitting in active site.

3.6 GROWTH AND REPLICATION OF POLYMER PARTICLE

The growth of the polymer particle has aroused much interest in both axademic and industrial laboratories. The reasons are twofold : on one hand, it was fell that if we understood the mechanistic path by which olefin is converted in polymer particles, then our knowledge of Ziegler-Natta catalysts will be more complete. We might, for example, learn how active centers distributed on the surface of the catalyst.

The second reason was more practical and of much importance for the commercial producers of polyolefins. The industrial motivation stemmed from the observation that heterogeneous Ziegler-Natta catalysts are uniquely capable of replicating their morphology into the morphology of the progeny polymer particles. This discovery was very important because it enabled workers to easily control the polymer particle morphology by controlling the morphology ot the transition metal salt, such as $TiCl_3$. By morphology, we mean the size, shape, density, snd texture which the particle has.

During the formation of the polymer, the $TiCl_3$ particle becomes dispersed throughout the polymer particle. The architecture of the $TiCl_3$ particle is largely determined by the method used for its synthesis. Secondary $TiCl_3$ particles formed by reduction of $TiCl_4$ with aluminum alkyls can be very large (40 μm) but they are in fact comprised of many much smaller primary particles, about 0.01 to 0.1 μm diameters. Growth of the polymer takes place on these primary particles, and they remain within the same polymer particled because the formed polymer acts to cement them. Several substructures have been identified. How the polymer chains are assembled to form the substructures and eventually the optically visible polymer particle is not yet completely understood. The whole particle consists of substructured that are formed polymer chains by one or more paths. Very probably, the paths by which polymer chains are assembled are affected by the catalyst surface, the mechanics of growth and crystallization, and external conditions such as stirring.

3.6.1 Changes during polymerization

On the basis of their kinetic studies, Natta suggested that, under the mechanical action of the growing polymer chains, the loosely held aggregates comprising the large α-$TiCl_3$ particles were broken up into the smaller crystalline particles [101]. The same forces were said to continue to cleave the smaller crystallite into still smaller particles. As mentioned, the disintegration of these smaller crystallites is presumed to tale place by cleavage along the loosely held chlorine-chlorine

Mechanical grinding can result in catalyst cleavage and a concomitant increase in catalyst activity; this was also demonstrated by Vecchi and co-workers [102] They reported that mechanical grinding of a $TiCl_3$ increased its surface area from 10 to 40 m^2/g and that the activity of the catalyst was simultaneously increased. In accordance with Natta's finding that the steady state was not changed by grinding the $TiCl_3$ sample, the above represents only the changes in the initial activities of the catalysts.

Stauffer workers recognized first the significance of the relationship between disingtegration of catalyst particles and how progeny particles are formed. They reported that polymer growth occurs on the individual smaller crystals in such a way that the polymer growth seems to be uniform through out the mass of the particle. They calculated that for reasonably high conversions, the volume of the polymer particle was about seven times greater than the volume of parent catalyst, but otherwise the shape and density of the progeny polymer particle was a faithful replica of the parent catalyst.

According to Hock [103] the active centers of the δ-TiCl₃ are found in the primary particles. When polymerization takes place, then primary particles become separated and the voids become filled with polymer. This polymer acts as a cement keeping the primary particles and formed polymer instact. What use to be an optically visible secondary particle now becomea larger catalyst polymer particle. Hock showed that at sufficiently high conversions, the primary particle become uniformly dispersed throughout the catalyst polymer particle. Berger and Grieveson [104]. From their study of ethylene polymerizations catalyzed by AlEt₂Cl - δ-TiCl₃ observed under an optical microscope that the outer surfaces of the catalyst-polymer particle still had strong purple color of TiCl₃ after the polymerization commenced. They concluded that the catalyst particles were not completely occluded in the layer of pure polymer byt, rather, as the polymer grew it entraind the catalyst. this picture is consistant with Hock's view.

When ethylene and propulene are polymerized with heterogeneous catalysts below 90 to 100°C, the polymer chains which from at the reaction centers crystallize into solid particles. If higher temperatures are used, e.g. 130 to 200°C, both highly linear polyethylene and isotactic polypropylene remain in solution.

3.6.2 Polymer chain assemblage

The picture that has emerged is not complete, and this account represents only an interim report. The particular experimental work required is difficult to do, and the findings are difficult to interpret unequivocally. Anomolies occur frequently. Each worker has examined some aspect of the problem and has given his view of what is happening. The findings are similar pieces of a puzzle which are coupled to form the whole picture; only here, some critical pieces are still missing. Yet, considerable progress has been made which deserves comment.

The different proposals that have been made to explain how polymer chains become assembled to form the larger morphological structures will now be discussed. From physical measurements on the polymer particle, two different models have been suggested : the extended chain fibril model and the folded chain fibrillar crystal model. According to the extended chain model as initially proposed by Ingram and Schindle [105] Chanzy, Day, and Marchessault [106] the polymer chains are formed and crystallized nearly simultaneously. Thus, the fibrils that form from the catalyst surface consis of aggregates of extended chains. Chain folding is absent and thus the lamellar crystallite does not form. As evidence for this morphology, the higher melting point of the particle polyethylene was cited in comparison to a polyethylene that has a lamellar (chain folding) structure (138° to $140\ ^{o}C$ vs $130\ ^{o}C$). Also cited were a narrower melting region in the differential thermal analysis curve and the absence of small angle X-ray maxima, which is characteristic of a lamella. Thermal treatment of the particle polymer below its melting point converts it at least in part to the lamellar structure. But streching polyethylene that has lamellar sturcture leads to an extended cahin structure.

These two early proposals are important because they focused on the extended and folded chains as basic building units for the various higher structures which form the polymer particle. Several important questions are logically raised. What are these higher structures? What is the sequence of thier formation? How do they combine to

form the next larger aggregate? What is the role played by the catalyst surface in determining if chain folding or extended chain takes place preferentially and in the formation of the larger structures? Does the aggergation process itself create forces which alter the morphology of the polymer chain? How about factors such as temperature of polymerization and the solvent that is used? It is questions such as these that recent publications have tried to answer.

Keller and Willmouth [107] compared fibrils present in the polyethylene particle with those found in polyethylene crystallized from stirred solution. They concluded that both extended chain and chain folded structures were present in both matcrials. Two possible mechanisms were offered for growth during polymerization. According to one proposal, the fibrils in the formed particle are flow-induced. In the alternative mechainsm, chain folding is explained in terms of unequal growth rates of molecules from a cluster of active sites (Figure 3.6)

In accordance with the latter scheme, the proximity of growing chains will determine the structure of the fibrils. If the chains are distant, crystallization will involve chain foding. If the chains are in close proximity, crystallization will favor extended chains. This means that, even with soluble catalysts, crystallization of extended chians can occur if the concentration of chains is high enough. Because active centers in Ziegler-Natta catalysts appear clustered on lateral faces and defects, the concentration of chain is favored.

Guttman and Guillet [108] proposed a model on the basis of observations made when propylene was subjected to a vapor phase polymeriztion with the $AlMe_3$. α $TiCl_3$ (Figure 3.7). According to their view, the rate of polymerization is initially more rapid than the rate of crystallization, resulting in an initial structure having the shape of a hemispherical mass of amorphous polymer. As the size of this globule increases, the rate of polymerization decreases, and, at this time, crystallization occurs at the apex of the globule in the form of folded chain lamellae.
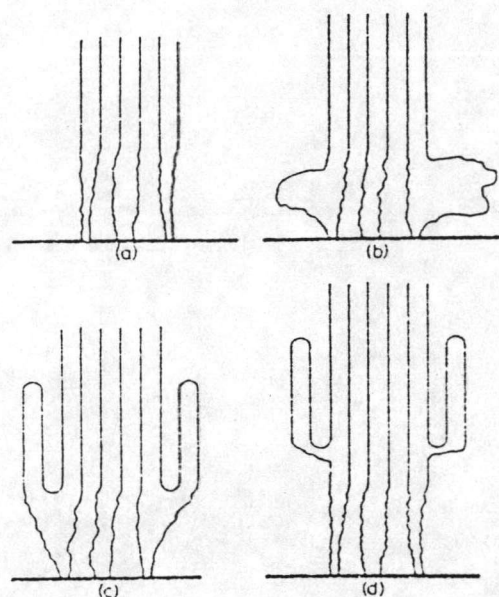
Figure 3.11   Different growth patterns suggested for polymer chain by
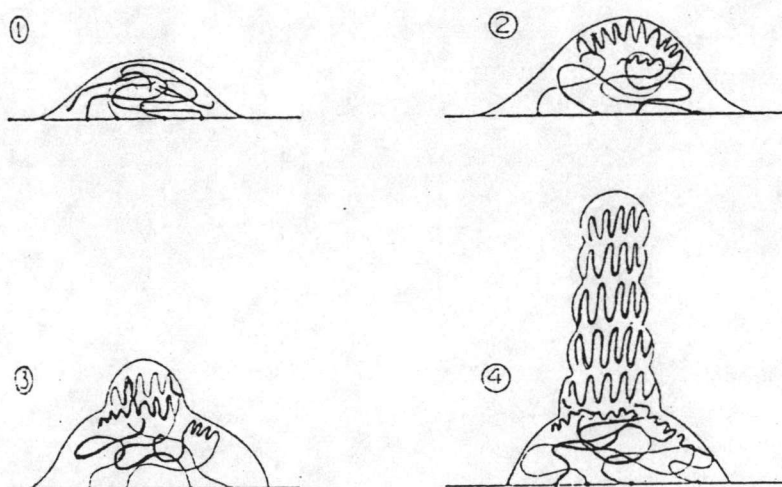Keller and Willmouth

Figure 3.12 Formation of fibrils during Ziegler-Natta polymerization as
proposed by Guttman

(a) Fractured polypropylene fibrils

(b) Proposed mechanism of fibril growth

A reasonable unifying scheme has recently been proposed by Wrister [109] to the many degrees of order in a polymer particle (Figure 3.8). The consecutive structures according to his order are : polymer coil (d = 6.4 A^O), fibril (400 A^O) which consists of filaments and lamellae (100 A^O thick), fibers (d = 5000 A^O), subparticles 20 to 70 μm, and particle (60 to 500 μm).
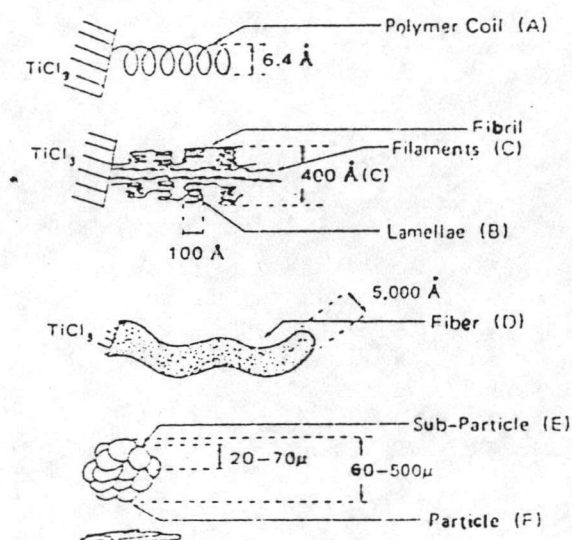
Figure 3.13   Consecutive levels of order in a polyolefin particle

Wristers suggested that the fiber is the basic morphological structure in polyolefin powders made with the heterogeneous Ziegler-Natta catalyst and that the primary particle was responsible for the fiber structure.

According to Wristers, more than one primary particle of TiCl3 was responsible for the formation of a fiber. As evidence, he pointed out that fibers had branches. Not all primary particles had equivalent activities. Polymer growth from the surface of the primary particle was said to occur only in a limited number of quadrants, and thereby the primay particle was not densely encapsulated. Wristers explained the easy removal of TiCl3 residues from the polymer particle by this model. For example, 90% of TiCl3 was removed in 30 minutes by contacting the polymer with alcohol. Also, removal of the TiCl3 from the polymer was not affected by increased efficiencies.

Wristers' findings strongly suggest that the basic morphological fiber structure is present in the polyolefin products that he prepared. Indeed, this work also pointed to the importance of primary particles in the formation of the fiber.

Other workers held that, in addition to any affect which the catalyst surface may exert, factors such as heat of polymerizatio, stress and compression forces, solvent, temperature of polymerization, and stirring also contribute their affect. The observed morphology was, accordingly, due to the composite action of all of the factors, and it is understandable that variations in observed morphology would occur because of differences in procedures used for the polymerization.

Boor agreed with Chanzy and co-workers in that the forces of polymerization leave polymer chain segments that are close to reaction center in a partially swollen or fused state. Due to the heat of polymerization, local hot spots near the center may exist. Only the further removed (and cooler) segments can crystallize. The crystallization can induce stretching on the segments closer to reaction centers and cause them to crystallize in an extended form. If the polymerization is done at higher temperatures (100 vs. $25^{\circ}C$) and in good solvents (toluene vs. heptane), then there is an opportunity for the polymer to dissolve and then recrystallize. Depending on the degree of stirring, extended chain formation and/or chain folding will occur. Also, chain transfer by metal alkyl molecules will release the polymer chain from the catalyst surface and leave it in a more independent position, not necessarilly aligned with the chains fixed to the surface by Ti-C bonds. These chains can crystallize from their vantage position.

3.7 PRACTICAL CONCURENCE

Control over catalyst (hence polymer) particle morphology an be very important in an industrail process. Thisis briefly decribed as

3.7.1 Effect on polymerization kinetics

A number of workers speculated that once the polymer forms and encapsulates the active center, the passage of olefin to these centers will be diffusion-limited. If, however, the catalyst particle is porous, then the polymer particle is porous and passage of olefin to the center will be enhance. Porosity would appear to be an polymer particles get larger.

3.7.2 Productivity in the reactor

Economics dictates that indudtrial reactors have a limiting size and require a certain residence time that the catalyst particle remains in the reactor. It is clear that the production of polymer would increased as the concentration of polymer particles in the reactor increases. Thus, the greater the bulk density of the polymer powder, the greater the throughput of polymer through the reactor. It do not matter whether the process is bath or continuous. Polymer powders that are highly dense usually have a regular shape and tend to have higher bulk densites. Normally, polyolifins are sold as nibs (short fused cylinders of polymer). For some applications, powders that have a specific bulk density and other morphological characteristics might be preferred.

3.7.3 Catalyst removal

Wristers found that rate of removal of $TiCl_3$ was independent of the amount of polymer associated with the catalyst. He concluded that the primary catalyst particle is responsible for the fiber structure and accounts for the ready removal of catalyst residues from the finished polymer particle.

3.8 KINETIC CONSIDERATION

A unified, universally accepted kinetic picture has not yet emerged, in spite of many excellent experimental and theoretical studies that have been done on this elusive catalyst. A kinetic phenomena exists that is the result of a delicate interplay between a number of operational factors that can be controlled during the synthesis of the catalyst and its use in polymerization. Such factors include the choice of catalyst components,

their absolute and relative concentration and use, etc. . Of course, these operational factors decide the nature and magnitude of basic kinetic parameter : structure, concentration and stability of active centers, lifetime of the growing polymer chains, the morphology of the catalyst-polymer particle in a heterogeneous polymerization, etc. .

While the effects of operational factors have been fairly well identified, the evaluation of basic parameters has been subject to considerable interpretation and hence, debate. And thereinlies the problem. Because of the experimental difficulties in measuring the value or contribution of individual parameters, their true effect in a polymerization is generally not well established. Often worker assumes, without firm evidence, the contribution of a parameter to remain contant or negligible in order to simplify the kinetic treatment.

3.8.1   Polymerization Rate Curve

A plot of the measured rate of polymerization of a monomer vs the time of polymerization constitutes a typical polymerization rate curve. Rate curves having different shapes have been found for Ziegler-Natta polymerization. Two type of rate curves are identified for discussion purposes : a contant-rate type and decaying-rate type.

The contant-rate type : the rate of polymerization gradually increased to a constant value that was maintain for at least 27 hours. The initial period was designated as an   " induction period".

The decaying-rate type : As in the constant-rate curve, threre is an induction period before a maximum rate is reached, and then the rate continues to decline with time.

Combination type : Another type of a polymerization rate curve had features of both type. When the same α-TiCl$_3$ was mechanically crushed quickly above the steady-state rate but immediately declined to the steady-state value.

Despite of typical rate curve, the actual rate vs time relationship will vary considerably according to the catalyst-monomer system. Thus, induction period (or the eary part of the curve) can vary from several minutes to hours. Also, while a few systems hold a constant stationary rate for a long time, as show in table 3.4, others

maintain a constant rate for only short period before a decline is observed. Some catalyst monomer systems show a faster decline in the polymerization rate than others.

Table 3.9 Selected Examples of Constant and Decaying Polymerization Rate Curves.

Catalyst	Monomer	Polymerization	
		^{o}C	hr
Constant polymerization rate curve		70	30
AlEt$_3$-αTiCl$_3$	Propylene	30	5
Al-i-Bu$_3$-VCl$_3$	4-Methyl-1-pentene		
Decaying polymerization rate curves			
AlEt$_3$-TiCl$_3$AA	Propylene	44	2
AlEt$_2$Cl-VCl$_4$	Ethylene	30	2
AlEt$_2$Cl-TiCl$_3$AA	Propylene	50	6
AlEt$_3$-αTiCl$_3$	Propylene	-	1-2
AlEtCl$_2$-αTiCl$_3$ .Donor	Propylene		
ZnEt$_2$-TiCl$_3$	Propylene		
AlEt$_3$-VOCl$_3$	Propylene		

To elucidate the difference of the polymerization curve, variuos stages were considered.

3.8.1.1 Induction period

This part of the curve has also been described as the"build-up" or "adjustment" period. The initial increase in the rate curve may require only minutes, and at other time hours, depending on the catalyst-monomer systems. A number of events can occur : (1) the metal alkyl and transition metal sureface react to from active centers;(2) monomer diffuses from the gas cap to the liqquid phase and finally to the active centers;(3) polymerization take plaace; and (4) is a heterogeneous catalyst, the catalyst particle begin to break up, exposing new surfaces and allowing new center to form, etc. . The temperature in the vicinity of the center may become much higher than that of the reaction medium and if heat transfer is insufficient, chemical reactions and physical changes characteristic of higher polymerization temperature may occur to some extent.

Natta and Pasquon [66] demonstrated that the effect of mechanically grinding the α-TiCl$_3$ was to decrease the induction period. In effect, the higher the steady- state rate, the less time was required to reach it. Factor such as higher temperature, higher monomer concentration, and higher rate of formation of active centers can be used to increase the value of steady-state rate. Apparently, the break up of catalyst into small fragments is an integral part of this induction period.

Shorter induction periods were observed with TiCl$_3$'s contianing AlCl$_3$ such as TiCl$_3$ .xAlCl$_3$ posssibly, the mode of break up of these TiCl$_3$ followed different part, since their morphologies were different from the α-TiCl$_3$ type. there is strong evidence that the primary particles whic make up the TiCl$_3$ .xAlCl$_3$ particles are smaller than those which make up the α-TiCl$_3$ particle. They also have higher surface areas and more active.

3.8.1.2 Constant-rate period

Only a few catalyst-monomer systems have been reporetd that give this shape curve. The AlEt$_3$-α-TiCl$_3$ system reported by Natta and co-workers is a relatively low activity catalyst. Natta concluded that when the steady-state rate was reached (also called a stationary rate), the system achieved an equilibrium state, that is, the number of centers remained constant. For AlEt$_3$-α-TiCl$_3$, the steady rate R was maintained for over 27 hour. The value of R depended on the temperature of polymerization, monomer concentration, catalyst concentration, etc., and was altered by changing these reaction variables.

3.8.1.3   Decaying period

Most of the catalyst-olefin systems are of the decaying type, in which the rate curve reaches a maximum and then continues to decline. The rate of decline varies accroding to the catalyst-monomer system. It appears that at increased time of the polymerization, the decline in rate become smaller. The decline in polymerization rate has been attributed to a number of factor : (1) a decrease a number of active centers; (2) a lowering of activity of individual centers due to structural changes; and (3) a lowering of activity of individual centers due to a shortage of monomer in the vicinity of the center. This shortage is said to occur when the center become encapsulated in polymer, and the monomer has difficulty diffusing from the liquid through the polymer to the centers.

3.8.2 Production product

The "as obtained" polymer consists of a mixer of polymer chains that can be decribed basically by four parameters : (1) linearity (or segree of branching) : (2) mode of couping : (3) stereochemical structure ; and (4) molecular weight. Not all polymer chain are alike, and variations in any of these parameters may occur. Because the property of the polymer depend closely on these parameters, much effort has been made to elucidate their kinetic and chemical origin.

3.8.2.1 Linearity

Branching can occur in the synthesis of polyethylene if competing side reactions form low molecular weight olefins (such as dimers, trimers), which then copolymerize with ethylene. Dimerization reactos involving propylene of higher olefins do not occur under normal conditions of polymerization, and similar interfering copolymerizations are absent.

3.8.2.2 Mode of coupling

The predominating coupling mode in polymerization of α-olefin is head-to-tail. Under certain conditions, however, head-to-head coupling can occur such as in

the synthesis of partially syndiotactic polypropylene [80] and in copolymers of ethylene and propylene [8] .

3.8.2.3 Stereoregularity

When the "as prepared" whole polymer product contains more than one steric structure, it is necessary to establhish whether this product is a mixture of polymer chains, each containing only one of the structures, of whether two or more structure are present in a single chain. If the formal is true, then seperation of the different structures can often be made by solvent fraction. Similar attemptsion the second type will lead to fractions having identical composition.

By doing these fractionations with a series of solvents at increasing temperature, fraction of different steric compositions can be isolated, and a stereoregularity distribution can be established for the catalyst-monomer systems. This was done for isotactic polypropylene.

To control steroregularity in the both α-olefin and diene polymerization, various factors such as the choice of catalyst (specific combination of metal alkyl and trasition metal salt), nature of the solid transition metal salt (crytal structure and composition), added electron donors, etc. can a significant role.

3.8.2.4 Molecular weight

Relative to the heterogeneous catalysts. Soluble catalysts produce polymer consisting of chains whose molecular weights are not significantly different from one another. They have a narrow molecular weight distribution (MWD). While in recent years gel permealtion chomatography has been used to measure MWD, most ofthe literature refers to the ratio $Q = \overline{Mw} / \overline{Mn}$ as a measure of dispersity of molecular weight (Mw and Mn are the weight average and number average molecular weights, respectively).

For soluble Ziegler-Natta catalysts, Q values in the rang 2 to 4 have been reported for polyethylene. In contrast , heterogeneous catalyst produce polymers that have much wider MWD, for example, Q > 4 to 20 or higher.

The reason for wide MWD in polymers prepared by heterogeneous catalyst are not well understood, and, for the present, these should be considerd as proposal. The cite reason are : (1) not all of the active centers become active at the same time;

(2) the active centers have a range of propagation rate constants [15]; (3) the value of propagation and termination rate constant change as the length of the polymer chain increased; (4) chain grow at a center is slowed down as the center becomes more and more encapsulated in the polymer mass. Olefin concentration at the center becomes decreasingly lower because the olefin find it difficult to pass through the polymer mass; and (5) the lifetime of growing chain increase as the center become more encapsulated because it is less susceptible to chain transfer by metal alkyl. The metal alkyl, being polar, find if even more difficult to diffuse to center through the polymer mass than the olefin.

3.8.3 Kinetic Treament of Polymerization Rate

Most of the catalyst system of Ziegler-Natta type are of a heterogeneuos nature and reaction proceed on solid surfaces. In these case, adsorption process are undoubtedly step in the reaction mechanism, as was pointed put rather early by Eirich and Mark [55] . It is often assumed that an adsorption equilibrium and will be maintain throughout the polymerization. This assumption implies that the rate of polymerization will be the rate-detemining step. Two basic mechanisms are possible which differ in the state of the reacting monomer.

(1) If it is assumed that propagation ocurrs only when both the alkyl aluminum compound and the monomer are adsorbed on the surface of the $TiCl_3$ lattice, a simple Langmuir-Hinshelwood mechanism applies. Generally, the rate of polymerization is then given by

$$Rp = Kp\theta_M\theta_A [S] \qquad (Eq. 3.21)$$

$$= \frac{KpK_MK_A[M][Al][S]}{(1+K_M[M]+K_A[Al])^2}$$

when the subscripts M and A refer to monomer and the alkyl aluminum compound. θ represent the fraction of the total active surface [s] covered, and K is the equilibrium constant of adsorption. The concentration [M] and [A] are those of monomer and aluminum compound in solution, and the value of [S] is proportional to the amount of $TiCl_3$ present in the system. Since it is very likely that the organometallic compound will be much more strongly adsrobed than the monomer, Eq. 3.21 can be simplified to

$$Rp = \frac{KpK_MK_A[M][Al][S]}{(1+ K_A[Al])^2} \qquad \text{(Eq. 3.22)}$$

In these case the propagation reaction will be first order with respect to monomer and will be slow a maximum in the rate as the concentration of the alkylaluminum compound increases. With a very strong adsroption of the alkyl aluminum compound,

$$Rp = \frac{KpK_M[M][S]}{KA[Al]} \qquad \text{(Eq. 3.23)}$$

(2) If the propagation reaction takes place between the unadsorbed monomer and adsorbed organometalic compound, the rate depedence with respect to the adsorbed organometallic compound will be give by Langmuir isotherm. The dependence upon monomer concentration may be described by mean of the Rideal mechanism. For a frist-order dependence with respect to monomer, the rate of polymerization will be given by

$$Rp = \frac{KpK_A[Al][S][M]}{(1+ KA[Al])} \qquad \text{(Eq. 3.24)}$$

In this case the rate will increase with an increase in the concentration of aluminum compound at its higher value. Mark [82] reported that at low rang of alkylaluminum concentration, the initial rate was proportional to the concentration of alkylalminum compound.

The Rideal and Langmuir-Hinshelwood model consider an adsorbed alkylaluminum compound to be the active center. Kinetic models have also been developed whereby the active center is an alkylated transition metal salt.

Burfied, McKenzie, and Tait [83] consider the rate to be as shown in Eq. 3.25

$$Rp = Kp\theta_MC_0 \qquad \text{(Eq. 3.25)}$$

Where K_P is the propagation rate constant with respect to adsorbed monomer, θ_M is the fraction of surface covered by adsorbed monomer, that is, ($\theta_M = K_M[M] / (1+K_M[M]+K_A[A])$); and C_O is the concentration of active centers taken to be alkylated trasition metal.

One characteristic feature of the Langmuir-hinshelwood rate law is that a maximum should be obtained in the polymerization rate curve as the concentration of metal alkyl increased. The reason for this that the metal alkyl and the monomer compete for adsorption with the available centers, When the concentration of AlR3 is high, these centers complex more favorably with the polar AlR3 and become less available for complexing with the hydrocarbon monomer. In contrast, according to the Rideal model, the monomer comes directly from the solvent or the gas phase. In the latter case, Rp will be independence of AlR3 concentration at high concentration levels. Measurement aimed at understanding both the type of center and then concentration at various stages of the polymerization have received considerable attention. Data of this type would permit eludication of the kinetic results with respect to the polymerization rate curve and the polymerization product.

The large variation in reported active center can be attributed to the different methods of measurements.

(1) All metal-carbon bonds present in the reactor at the time of termination are assumed to be active centers. Chain transfer by metal alkyl is rejected.

(2) Chain transfer is accepted, extrapolate metal-carbon concentration to zero time, and take the extrapolate value to be the site number.

(3) The total adsrobed metal alkyl is considered as a measurement of active centers.

(4) The assumption being made that the rate of chain transfer is proportional to the number of active sites, $R_P = K_{tr}[M][Al][C^*]$. From the rate transfer reaction $[C^*]$ is calculated.
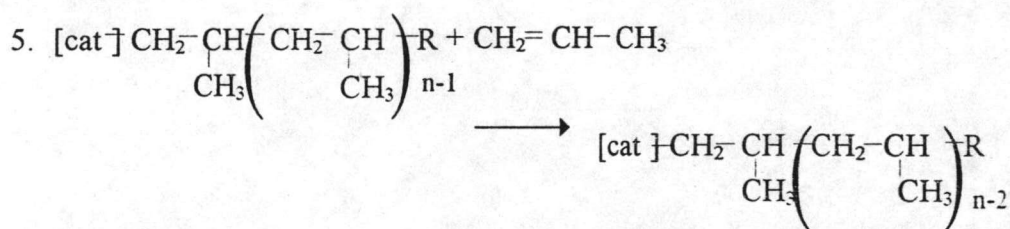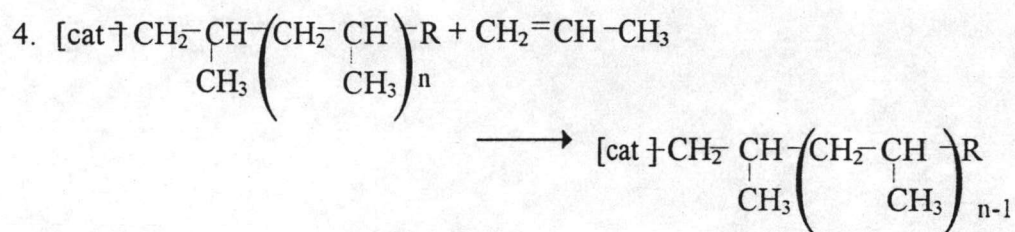
3.8.4 Kinetic Schemes

An addition polymerization, be it radical, cationic, or anionic, usually involves three different steps initiation, propagation and termination. The Ziegler-Natta polymerization can also be described in this way, and the following reaction were proposed by Natta and co-workers [84] as possible for the three steps.

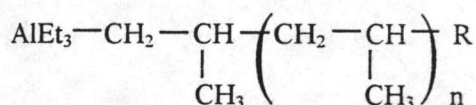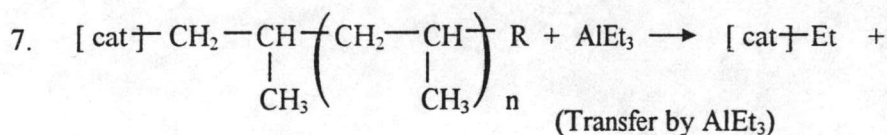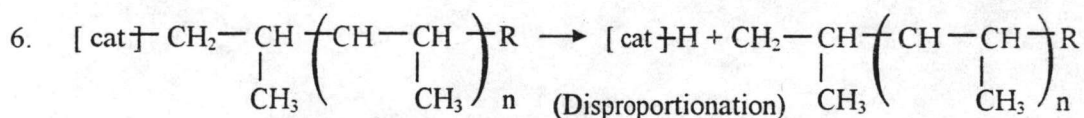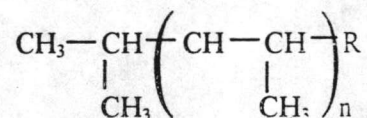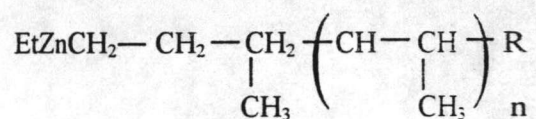**Table 3.10 Kinetic Scheme Proposed by Natta and co-workers.**

Initiation

1. $[\text{cat}]\text{H} + CH_2=CH-CH_3 \longrightarrow [\text{cat}] C_3H_7$

2. $[\text{cat}]C_2H_5 + CH_2=CH-CH_3 \longrightarrow [\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}-C_2H_5$

3. $[\text{cat}]C_3H_7 + CH_2=CH-CH_3 \longrightarrow [\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}-C_3H_7$

Propagation

4. $[\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)_n R + CH_2=CH-CH_3$

$$\longrightarrow [\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)_{n-1} R$$

5. $[\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)_{n-1} R + CH_2=CH-CH_3$

$$\longrightarrow [\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH_2-CH\underset{\underset{CH_3}{|}}{}\right)_{n-2} R$$

Chain Termination

6. $[\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH-CH\underset{\underset{CH_3}{|}}{}\right)_n R \rightarrow [\text{cat}]H + CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH-CH\underset{\underset{CH_3}{|}}{}\right)_n R$

(Disproportionation)

7. $[\text{cat}] CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH_2-CH\underset{\underset{CH_3}{|}}{}\right)_n R + AlEt_3 \longrightarrow [\text{cat}]Et +$

(Transfer by AlEt₃)

$$AlEt_3-CH_2-\underset{\underset{CH_3}{|}}{CH}\left(CH_2-CH\underset{\underset{CH_3}{|}}{}\right)_n R$$

8. $[\text{cat}]-CH_2-CH(CH_3)-(CH_2-CH(CH_3))_n-R + CH_2=CH-CH_3 \longrightarrow [\text{cat}]-C_3H_7 +$ (Transfer by monomer)

$$CH_2-CH(CH_3)-(CH_2-CH(CH_3))_n-R$$

9. $[\text{cat}]-CH_2-CH(CH_3)-(CH_2-CH(CH_3))_n-R + ZnEt_2 \longrightarrow [\text{cat}]C_2H_5 +$ (Transfer by $ZnEt_2$)

$$EtZnCH_2-CH_2-CH_2(CH_3)-(CH-CH(CH_3))_n-R$$

10. $[\text{cat}]-CH_2-CH(CH_3)-(CH_2-CH(CH_3))_n-R + H_2 \longrightarrow [\text{cat}]-H +$ (Transfer by H_2)

$$CH_3-CH(CH_3)-(CH-CH(CH_3))_n-R$$

The notation [cat]-R was used to Natta to designate the active center taken to be a metal-carbon bond. R can be a polymer chain (R = Pn) a hydride (R = H) or an alkyl (R = methyl, ethyl, ... ect.). or suitable moiety. As long as R is one of the above, the center is active or can become active. If, however, R become a halogen, sulfur, nitrogen, or oxigen, then the center is no longer active for the polymerization of olefins, dienes, etc. .

In this sheme, the active metal could be a transition metal (now accepted by most workers to be the case) or a base metal (previously considered valid by many works but now by only a few). The Natta kinetic scheme is shown in the following for the polymerization with the $AlEt_3$-$TiCl_3$ catalyst and with $ZnEt_2$ or H_2 also being present as transfer agents. Having these equations together will be helpful in the evaluation of the kinetic data. In all of these termination reactions, chain growth stops, but the [cat] -R center remains active for further polymerization.

Adventitious or added impurities may also react with the [cat]-Pn center and, in this case, termination of chain growth will be accompained by inactivation of the center, as shown in Eq. 3.26.

$$[cat]CH_2\text{-}CH(CH_2\text{-}CH)_nR + ROH \quad [cat]\,OR + CH_3\text{-}CH(CH_2\text{-}CH)R$$
$$CH_3 \quad CH_3 \qquad\qquad\qquad CH_3 \quad CH_3$$

Dead

center (Eq. 3.26)
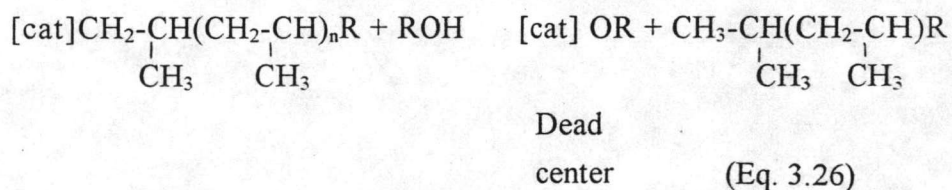
3.8.5 Rate Determining Step

It has generally been accepted that the involves two steps : (1) the complexing of the monomer at the metal-carbon center and (2) the insertion of monomer into the metal-carbon bond. A common characteristic of all Ziegler-Natta catalysts is the dependence of the polymerization rate on concentrations of the transmition metal salt and the monomer. This in itself, however, does not reveal whether k_1 (the complexation step) or k_3 (the insertion step) is the rate-determining step. Many workers argue that only fraction of the total available centers are complexed with the monomer at a moment, because a frist-order rate dependence is experimentally observed over a wide rang of monomer concentration. If the rate-determining step was step 1, then $k_2 \gg k_1$ (monomer) > k_3 . Cossee [85] has reached this conclusion in the following way : under steady-state condition $d(MA)/dt = 0$ and

$$-\frac{d[M]}{dt} = \frac{k_1 k_2 [C][M]}{k_1 [M] + k_2 + k_3} \qquad \text{(Eq. 3.27)}$$

where $C = [MA]+[A]$, and $[A]$ = all vacant sites = $\Sigma[A]$ (the active center is an alkylated transition metal). The observe dependence of the polymerization rate on monomer pressure requires either $k_2 \gg k_1[M]$ or $k_3 \gg k_1[M]$.

If every complexed monomer would be instantaneuosly inserted, then $k_3 \gg k_1$ [M]. Cossee argue against this view on the grounds that the measure activation energy ($E_a = 11$ to 14 kcal/mole) is too high to account for putting a neutral olefin molecule into a vacant position. He prefers to attributed this higher E_a value to a rearrangment-insertion step.

In term of theCossee mechanism, the polymerization rate R_p is expressed in Eq. 3.28.

$$R_p = (k_1 k_3 / k_2)[C][M] \qquad \text{(Eq. 3.28)}$$

and the measured activation energy ΔE is

$$\Delta E = \Delta E_R - \Delta H_C \qquad \text{(Eq. 3.29)}$$

where ΔE_R is the activation energy for the rearragement and ΔH_C is heat of complex formation (assumed to be small) and therefor $\Delta E = \Delta E_R$.

Schindler [86] on the other hand, argued in favor of the adsorption step being rate-limiting. This view was reached from the effect of inert such as N_2 or ethane on the polymerization of ethylene in the presence of catalysts such as $AlEt_2Cl$ / $AlEt_2H + TiCl_4$. He observe that the rate of polymerization was depressed more than would be proportional to the decrease in the partial pressure of ethylene. Schindler concluded that these "inert" gases are adsorbed on the active centers and depress activity. Relative to ethylene, nitrogen, ethane are less strongly held. In the true adsorption - desorption equilibrium, the number of centers complexed by nitrogen or ethane relative to ethylene would be expected to be relatively smaller. But under the conditions of a very fast propagation of the complexed ethylene and a slow rate of adsorption, the number of active sites blocked by adsorbed ethane or nitrogen was considered to be much higher than by ethylene, even though the latter is more strongly adsorbed.
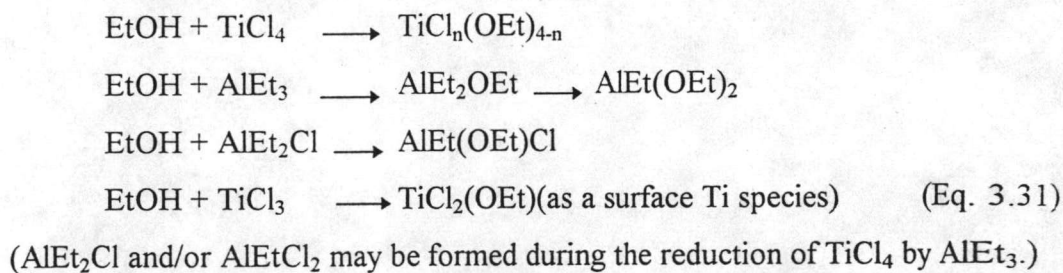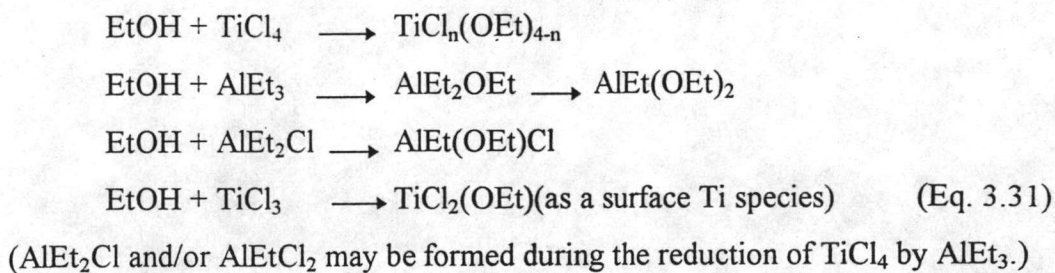
3.9 Modification of Ziegler-Natta Catalysts by Third Components

Most of the third components cited in the literature can complex or react with aluminum alkyls[2,3]. When they also complex or react with the transition metal salt or with the reaction by-product formed when the aluminum, alkyl and the transition metal salt react, several equilibria or reaction paths are possible. Consider, for example, the following complexs formed when Et_3N is added to a mixture of $AlEt_2Cl$ and $TiCl_3$.

$$Et_3N + TiCl_3 \longrightarrow Et_3N \cdot TiCl_3 \text{ (as a surface complex)}$$
$$Et_3N + AlEt_2Cl \longrightarrow Et_3N \cdot AlEt_2Cl \text{ (in solution)} \qquad \text{(Eq. 3.30)}$$
$$Et_3N + AlEtCl_2 \longrightarrow Et_3N \cdot AlEtCl_2 \longrightarrow AlEt_2Cl + Et_3N \cdot AlCl_3 \text{(in solution)}$$

($AlEtCl_2$ can be formed during site formation, that is, alkylation by $AlEt_2Cl$ of the $TiCl_3$ species located on surface of the $TiCl_3$ crystallite.)

If the third component reacts with both the metal alkyl and transition metal salt, then the actual catalyst is a mixture of several reactants, as shown in Eq.

$$EtOH + TiCl_4 \longrightarrow TiCl_n(OEt)_{4-n}$$
$$EtOH + AlEt_3 \longrightarrow AlEt_2OEt \longrightarrow AlEt(OEt)_2$$
$$EtOH + AlEt_2Cl \longrightarrow AlEt(OEt)Cl$$
$$EtOH + TiCl_3 \longrightarrow TiCl_2(OEt) \text{(as a surface Ti species)} \qquad \text{(Eq. 3.31)}$$

($AlEt_2Cl$ and/or $AlEtCl_2$ may be formed during the reduction of $TiCl_4$ by $AlEt_3$.)

Depending on the concentration of reactants, mode of mixing, temperature and time of reaction and use in polymerization, and other factors, the working catalyst may have a variable composition. It is most difficult, if not impossible, in many of these cases to explain the role of the third component precisely.

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$$Et_3N + AlEtCl_2 \longrightarrow Et_3N \cdot AlEtCl_2 \longrightarrow AlEt_2Cl + Et_3N \cdot AlCl_3 \text{(in}$$

solution)

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3.9.1 The Different Ways that a Donor (or Reactant) Can Affect a Ziegler-Natta Polymerization

1. Isotactic Crystallinity in Polyolefins

The more crystalline a polymer, the higher was its tensile strength, the higher were the insoluble fractions in boiling heptane, the lower was the xylene soluble fraction, and higher was the flexural modulus. Electron donors usually increased the isotactic-regulating ability of a catalyst, but not always

2. Activity

Most frequently aclaim is made that the activity of the catalyst is increased. A variety of reactants or donors have been reported. The activity of the CH_3 $TiCl_3$ - $TiCl_3$ catalyst for polymerizing propylene was increased by n-Bu_3N [1]. The presence of ethylorthosilicate in a catalyst prepared by reduction of $TiCl_4$ with $AlEtCl_2$ and activated with $AlEtCl_2$ was reported to increase its activity, and a highly crystalline polypropylene having a high bulk dendity was formed [2]. Higher rates were claimed for polymerization of propylene when peroxides were added to $AlEt_3$ - $TiCl_3$ [3].

3. Copolymerization Behavier

The copolymerization behavior of a catalyst can be attered. An improved copolymerization catalyst was reported if VCl_3 was reacted with R_4NCl, as shown in Eq.   , and the product was combined with Al-i-Bu_2Cl [4]

$$VCl_3 + R_4NCl \longrightarrow R_4N^+(VCl_4 * HOC_2H_5)^- \qquad (Eq. 3.32)$$
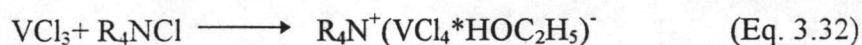
The molecular weight of ethylene-propylene copolymer was regulated by use of pyridine N-oxide when the catalyst $Al_2 Et_3 Cl_3$ - $VOCl_3$ was used [5]

4. Molecular Weight Control

Dost and co-workers [6] recogniged that electron donors can increase or lower molceular weights of formed polyethylene when added to Ziegler-Natta catalysts ; for example, aldehydes, esters and amines were added to the AlR_3 - $TiCl_4$ catalysts. The molecular weight distribution can be attered by presence of donors. Erofeev [7] reported that the width of the molecular weight distribution was narrowed by the presence of anisole in the $AlEt_2 Cl$ - $TiCl_4$ catalyst. This was attributed to diminution of low molecular weight fractions. M_W / M_n values 4.3 to 9.4 were observed, compared to valves 13 to 16 for unmodified catalyst

5. Microstructure of Diene Polymer

Carlson [8] showed that cis-1, 4 content and reaction rate in polybutadiene maximized at a certain concentration of water with the aluminum alkyl-soluble cobalt system ($CoCl_2$ - $AlCl_3$ + $AlEt_3$). Polymer molecular weight maximized when the concentration of water was greater than needed to achieve optimum cis-1, 4 content and reaction rates

6. Other Changes

Better fabrication of bottles by blowing techniques was reported by Roberts [9] if NH_3 was present in the Al -i - Bu_3 - $\beta TiCl_3$ catalyst when used to polymerize ethylene. By complexing Al -i - Bu_3 -$TiCl_4$ with carbon black (catalyst was chemisorbed on its surface).

3.9.2 Selected Mechanistic Proposals

The change in the behavior of a catalyst has been explained by individual authors in a number of ways. Some of these are showed :

1. Inactivation of the Poison by a Donor

A poison is formed during site formation, and the donor removes this poison by complexing it. This argument was put forth by Count to explain the activating affect of inorganic halides (KCl) and electron donors (amines) when added to the $AlEt_2$ Cl - $TiCl_3$ catalyst [10]. Specially he proposed that third components complex and inactivate the poison $AlEtCl_2$, which was formed when $AlEt_2$ Cl and $TiCl_3$ were mixed.

Burfield and Tait [11] examined in great detail the effect of Et_3N on the polymerization at 4-methyl-1- pentene in benzene solvent in the presence of Vcl_3 + Al-i-Bu3 . The activating deactivating effect of Et_3 N was explained in the following way : activation at low amine concentration was due to the removal of all adsorbed chleroaluminum species from the catalyst surface, where they blocked potential active centers. The chloroaluminum alkyls were by-products of the site formation step which is shown by

VCl_3 + Al-i-Bu$_3$ → VCl_2-i-Bu + Al-i-Bu$_2$Cl (solution)   (Eq. 3.33)

VCl_3 + Al-i-Bu$_2$Cl → VCl_3* Al-i-Bu$_2$Cl (at surface centers) (surface blocked)

VCl_3* Al-i-Bu$_2$Cl + Et_3N ⟶ VCl_3 +Al-i-Bu$_2$Cl * Et_3N (solution) (surface free)
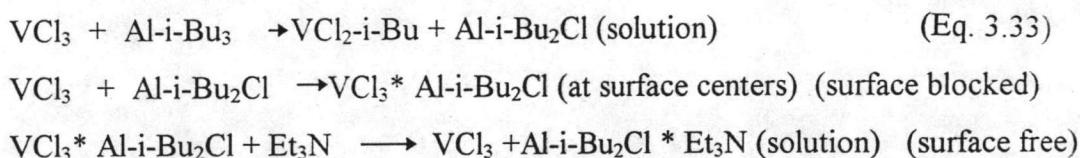
The first equation shows the formation of the active center i-BuVCl_2. Site formation is prevented when the surface of VCl_3 is complexed with the chloroaluminum alkyl. A similar role was suggested for excess Al-i-Bu$_3$, as shown in Eq

VCl_3* Al-i-Bu$_3$ Cl +Al-i-Bu$_3$ ⟶ VCl_3 +Al-i-Bu$_3$ * Al-i-Bu$_2$Cl   (Eq. 3.34)
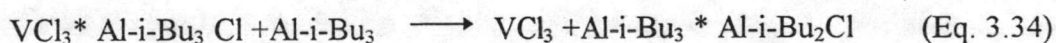
2. Lowered Concentration of the Metal Alkyl

An electron donor complexes the metal alkyl and decreases its effective concentration. Processes such as site formation and chain transfer reactions are affected. Vinogradov and co-workers [12] studied the effect of electron donors and acceptors on the polymerization of butadiene in the presence of the Al-i-Bu$_2$ Cl-CoCl$_2$ catalyst. They suggested that the effect of the additives was to shift the reaction as shown in Eq

$$2R_2AlCl \rightleftharpoons RAlCl_2 + R_3Al \qquad (Eq. 3.35)$$
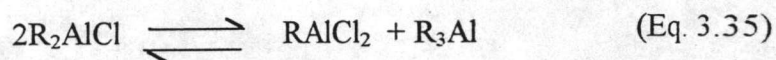
Those donors which shifted the equilibrium to the right (RSR, ROR,R$_3$N, KCl and NaCl) enhanced the reduction efficiency of the system. Consequently, the catalyst was less active, lower molecular weight polymers were formed, and 1, 2 - microsturcture was favored. But if donors were added that shifted the equilibrium to the left (such as AlCl$_3$, RAlCl$_2$, Br$_2$, H$_2$O, and aloxane of AlEt$_2$Cl), an increase in catalyst activity, an increase in cis-1, 4 structure, and higher molecular weight polymers were obtained.

3. Diminished Reactivity of the Metal Alkyl

When the metal alkyl is complexed with an electron donor, its coordination capacity is diminished and, consequently, the reactivity of metal-carbon bond is decreased. Bacskai [13] proposed this idea to explain the activity of the AlEt$_3$ - TiCl$_3$ - pyridine system for the copolymerization of propylene and 6-chlorohexene-1. The chlorine in 6-chlorohexene-1 reacts readily with uncomplexed AlEt$_3$ but not with the AlEt$_3$ pyridine complex.

4. Formation of the New Metal Alkyl

The third component reacts with the metal alkyl to generate a new metal alkyl ; for example

$$AlEt_3 + EtOH \rightarrow AlEt_2 Et + ethane \qquad (Eq.\ 3.36)$$
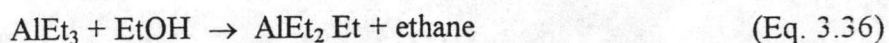
The catalyst may exclusively contain the new metal alkyl or a mixture of $AlEt_3$ and $AlEt_2 Oet$. Any compound that can react with the active metal-carbon bonds of the metal alkyl may act similarly, such as EtSH, COS, CS_2 O_2, RCHO, R_2CO, alkyl halides. If the reaction of the third component and the metal alkyl is in complete, then unreacted molecules may also react with the active centers (the transition metal-carbon bonds). Thus, a decline in rate due to the reactant may also occur in this way [14]

5. Formation of the New Catalyst.

Gippin found that, for the polymerization of isoprene with the Al-i-Bu-$TiCl_4$ catalyst ($Al/Ti \geq 1$), water and diphenyl ether acted synergistically in raising the catalyst efficiency. According to Gippin, these catlayst components react to form the real catalyst, as shown in Eq.

$$Al\text{-}i\text{-}Bu_3 + TiCl_4 \longrightarrow \beta TiCl_3 + Al\text{-}iBu_2Cl \qquad (Eq.\ 3.37)$$
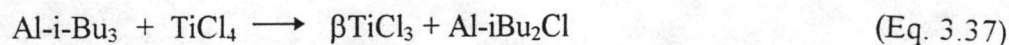
When the Al-i-$Bu_3/TiCl_4$ ratio is either less or greater than 1, lower efficiencies are obtained than if this ratio was 1. The maximum efficiency was obtained at lower ratios by the addition of diphenyl ether. When the ratio was 1.1, however, both diphenyl ether and water were needed to restore the maximum efficiency. Gippen stated that water acts to hydrolyze and deactivate the poison i-$BuTiCl_2$, which would form from the excess Al-i-Bu_3 when the Al-i-$Bu_3/TiCl_3$ ratio was 1.1 (According to him, i-$BuTiCl_2$ causes isoprene to form dimers, trimers, and low molecular weight

oils.) Diphenyl ether acts to complex Al-i-Bu$_2$Cl and thereby prevents the formation of higher Lewis acids by hydrolysis; for example, i-BuAl(OH)Cl or i-BuAl(Cl)-O-Al(Cl)-i-Bu. These other components were believed to be responsible for wanted gel formation and perhaps cyclization by a cationic mechanism. In developing a practical commmmercial process, the action of those components must be eliminated.

6. Deactivation of the Active Centers.

This explanation was discussed in detail in the type 2 case. Mezhikovskii and co-workers[69] examined the effect of water and alcohols on the polymerization of propylene when the AlEt$_3$-αTiCl$_3$ catalyst was used. Rather complex relationships were obtained when the rate of polymerization and isotacticity were measured as the concentration of water was increased. The observed induction period was attributed to adsorption of water on the surface of the αTiCl$_3$(sites were blocked). But as this adsorbed water was reacted with AlEt$_3$, and thereby removed from the surface of TiCl$_3$, the polymerization commenced. Because the adsorption was fast, the induction period was tantamount to the time required for the adsorbed water to be reacted off the surface by AlEt$_3$ molecules. The reaction product, AlEt$_2$OH, however, is also a poison and can be removed by reaction with additional AlEt$_3$ molecules. These workers speculated from their kinetic data that higher concentrations of water promoted the polymerization by stabilizing reaction centers, which they assumed to be trivalent alkylated titanium alkyl-aluminum complexes.

7. Activation of Dead Centers.

Under the condition of the polymerization, the active centers undergo reduction to a lower valence state metal species that are no longer active for polymerization of the olefin. The third component oxidizes this inactive species to a higher valence state compound, which is easily realkylated to form an active center.

Chirstman [81] examined the effect of a series of polyhaloorganic molecules on the activity of several soluble vanadium-based catalysts for the polymerization of ethylene at 120°C in some detail. In the absence of a promotor, yields were low. When promotor was added continuously throughout the polymerization, high yields of polymer per mmole vanadium were obtained.

8. Change in the Physical State of the Transition Metal Salt.

Some distinct schemes were suggested. Minsker and Bykhovskii [82] suggested that amine molecules that complexed on the surface of $TiCl_3$ facilitate the breakdown of the crystals along the plane of cleavage. By virtue of a grater surface area, more sites can form for polymerization of propylene.

Razuvaev, Minsker, and Chernovskaya [85,86] proposed that aromatic type electron donors in the $AlEt_3$-$TiCl_3$ catalyst (propylene) changed the energetic conditions at the surface of $TiCl_3$ and the strength of the $AlEt_3$-$TiCl_3$ complex. Compounds at concentrations of 0.2 to 3 moles per liter solvent increased activity but lowered polymer isotacticity and molecular weight . But in other experiments, they observed that ethers increased catalyst activities and molecular weights and proposed that the donor aids in the complexing of propylene at the center[87].

3.10 Termination and Chain Transfer

Termination of chain growth in Ziegler-Natta polymerization can be caused by specific reactants and complexing agents or by thermal clevage. Only a small number of these reactants are known that behave as transfer agents; that is they do not simultaneously destroy the transition metal bond center. Examples of transfer agents are H_2 and $ZnEt_2$, and these have become the practical agents for controlpolymer molecular weight in most olefin polymerizations.

Using Pn to represent the growing polymer chain, these reaction can be expressed in two ways : (1) those in which the active center is simultaneously killed, as shown in Eq. 3.38, where

$$Ti\text{-}Pn + BuCl \longrightarrow Ti\text{-}Cl + Bu\text{-}Pn \qquad (Eq.\ 3.38)$$

active   dead
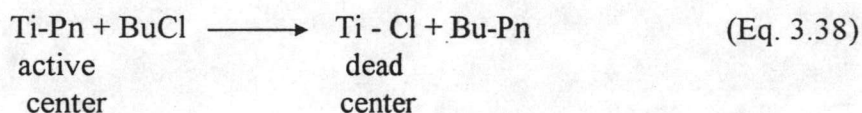
center   center

the active Ti-C bond is converted to an inactive Ti-Cl bond and Pn is exchanged for Cl and (2) those in which the active center continues to polymerize, as shown in Eq. 3.39.

$$\text{Ti-Pn} + \text{ZnEt}_2 \longrightarrow \text{Ti - Et} + \text{PnZnEt} \qquad \text{(Eq. 3.39)}$$

active   dead
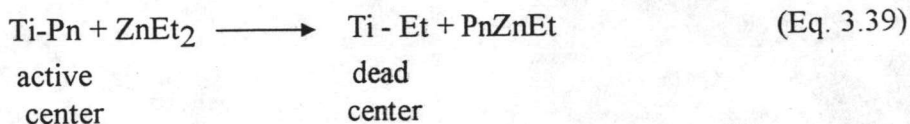
center   center

The polymer chain, Pn, becomes detached from the Ti center by exchange of Pn for Et.

3.10.1 Termination by organic and inorganic compounds

Typical compounds included alcohols, alkyl halides, alkane thiols, H_2S, $SnCl_4$, $SiCl_4$, NaCl and BCl_3.

In practice, none of these resulted in attractive molecular weight control agents, for two reasons. Firstly, in all cases the reaction center was simultaneously destroyed, with a concomitant decrease in catalyst activity. Only if the activity of the catalyst was very high could the lowering of molecular weight be justified by the loss in polymer yield. Secondly, a problem arose because the compound reacted so fast with the metal alkyl that little was available for termianation of chain growth. This reaction often resulted in the generation of the second metal alkyl that could function as a site former, and in the loss of trhe first metal alkyl. It is easy to see that any number of effects can be obtained, depending on the rateds of these reactions and the nature of the formed metal alkyl.

3.10.2 Termination by metal alkyls

Metal alkyls can act as terminators of chain growth and under suitable conditions, they function as true transfer agents. Natta and Pasquon [66] first recognized that in a polymerization of propylene with the AlEt - α-$TiCl_3$ catalyst the molecular weight decreased at higher concentrations of $AlEt_3$. To support their view that variations in molecular weight with $AlEt_3$ concentration were due to chain transfer with participation of the Et groups of $AlEt_3$, polymerizations were done with 14c-labeled $AlEt_3$ and the polymer was analyzed for radioactivity.

Natta and co-worker [67] later demonstrated that $ZnEt_2$ was a considerably more effective transfer agent when added to the $AlEt_3$-$TiCl_3$ catalyst and used of propylene polymerization. The process by which aluminum and zinc alkyls terminate chain growth was shown to involve alkyl exchange between ethyl groups of

the $ZnEt_2$ and the growing polymer chains on the active centers. Using Natta's notation, [cat] = the catalyst complex on which the polymer chain Pn is growing, the reaction may be represented as follows.

$$[cat]Pn + ZnEt_2 \longrightarrow [cat]\text{-}Et + PnZnEt \quad (Eq. 3.40)$$
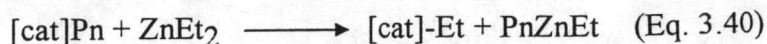
Its use left the question of the metal open int he active metal-carbon bond, thet is, Al-C or Ti-C in the $AlEt_3$-$TiCl_3$ system. The rate of this exchange reaction was first-order with respect to the $ZnEt_2$ concentration and was independent of the partial pressure of propylene. The formed Pn-ZnEt alkyl does not further participate in the polymerization. This view was supported by their observation that $ZnEt_2$ was consume during the polymerization. To obtain a polymer having a constant average molecular weight throughout the polymerizatioon, additional $ZnEt_2$ must be added to replace the consumed portion. Natta attributed the lower transfer ability of aluminum alkyls to t their being closely associated as dimers, where as $ZnEt_2$ exists in the undimerized form.

3.10.3 Termination by molecular hydrogen

As a terminating agent, molecular hydrogen is the most attractive it does not simultaneously kill reaction centers. It is a true transfer agent. Side reactions can occur that will affect catalyst activity. Natta [68] proposed that chain termination involves hydrogenolysis of the live metal-carbon bond centers, as shown in Eq. 3.20

$$[cat]Pn + H_2 \text{ -----> } [cat]\text{-}H_2 + PnH \qquad (Eq. 3.41)$$
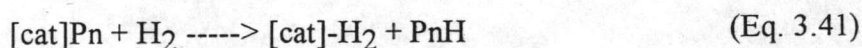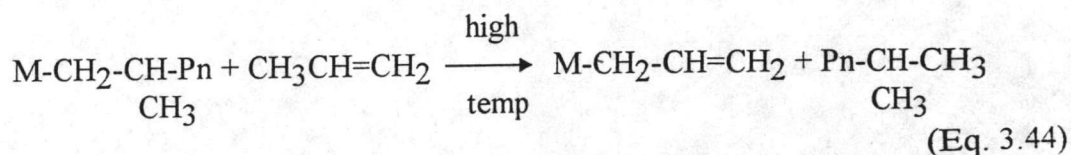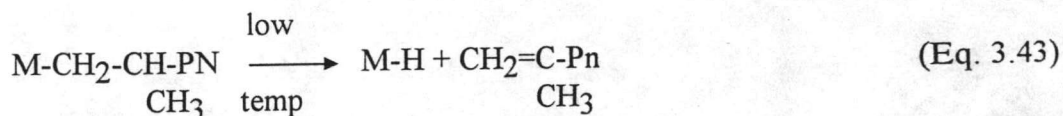
By infrared spectroscopy, they showed the presence of isopropyl end groups in the polymer when propylene polymerized. The active center (M-C bond) is regenerated (Eq. 3.21) when an olefin molecule adds to the M-H bond.

$$[cat]H + CH_3CH{=}CH_2 \longrightarrow [cat]\text{-}CH_2CH_2CH_3 \qquad (Eq. 3.42)$$
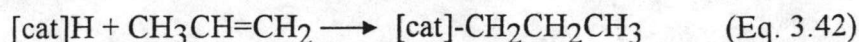
The patent literature strongly suggests that hydrogen is the preferred transfer agent for decreasing molecular weights of polyolefins. Without hydrogen, most catalyst processess would produce polyolefins that have too high a molecular weight for most practical applocations. The hydrogen method id inexpensive, easy to use, and does not leave a residue in the polymer.

3.10.4 Termination by thermal clevage

Two chain termination reactions have been postulated to explain the formation of vinylidene and vinyl and groups, as shown below.

$$\text{M-CH}_2\text{-CH-PN} \xrightarrow[\text{temp}]{\text{low}} \text{M-H} + \text{CH}_2\text{=C-Pn} \qquad \text{(Eq. 3.43)}$$
$$\qquad \text{CH}_3 \qquad\qquad\qquad\qquad \text{CH}_3$$

$$\text{M-CH}_2\text{-CH-Pn} + \text{CH}_3\text{CH=CH}_2 \xrightarrow[\text{temp}]{\text{high}} \text{M-CH}_2\text{-CH=CH}_2 + \text{Pn-CH-CH}_3$$
$$\qquad \text{CH}_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{CH}_3$$
$$\text{(Eq. 3.44)}$$

$$\text{M-CH}_2\text{-CH=CH}_2 \xrightarrow[\text{nC}_3\text{H}_6]{\text{propylene}} \text{M-CH}_2\text{-CH-(CH}_2\text{-CH)n-CH}_2\text{-CH=CH}_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{CH}_3 \qquad \text{CH}_3$$
$$\text{(Eq. 3.45)}$$
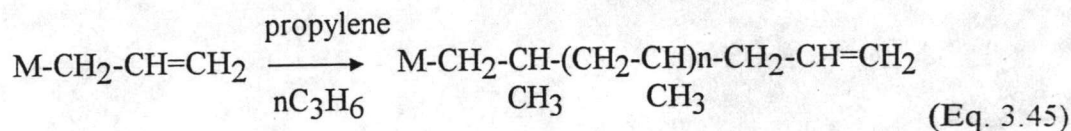
Longi and co-worker [69] showed that the ratio between vinyl and vinylidene end groups increased from 1.0 at 100°C to 2 at 200 °C. Spontaneous dissociation type of chain cleavage (Eq.3.22) apparently is insignificant for Ti-based catalysts at low polymerization temperatures, that is , below 60° to 80 °C.

3.10.5 Termination by mechanical forces

Kissin [70] presented evidence for his proposal that mechanical termination takes place during the stereospecific polymerization of propylene. Because mechanical termination is proportional to polymerization rate, it is not distinguish able from chain transfer through the monomer. Kissin suggested that the clevage of the metal-carbon bond occured during a temporary discontinuation of monomer addition at the center. This bond broke because of stretching of segments of the polymer chains in the crystallite bundles.

3.11 TITANIUM - BASED ZIEGLER - NATTA CATALYST

Because so much of the Ziegler-Natta literature is based on titanium compound. If the patent literature is an indication of the types if catalyst used in the commercial products of polyolefins, it is likely that $TiCl_3$-based catalysts are widely used. It' s important to recognize that the actual performance of a $TiCl_3$ modification can vary significantly according to the particular conditions of synthesis. For example, the initial and constant rate of polymerization will depend on the average size so the $TiCl_3$ crystallines because the surface of the latter

largely determines the number of active centers. The polymer particle shapes and sizes will depend on the sizes and shapes of the catalyst particles. The exact concentrations of reactants, made of mixing, temperature of reaction, etc., will determine the characteristics of the particular catalyst. The relationship of the chemical constitution and behavior of the initial components to catalytic activity and stereospecificity is demonstrated in the details.

3.11.1 Physical State of TiCl$_3$

Natta et al. have described the various crystalline modifications of TiCl$_3$, α, β, γ and δ forms. The α form shown in Figure 3.14 contains a succession of structural layers corresponding to a hexagonal close-packing to chlorine atoms. The titanium atoms are also distributed in layers, repeating every two layers of chlorine atoms perpendicular to the direction of the three-fold axis. The β form shown in the figure 3.15 consists of a hexagonal unit cell containing two TiCl$_3$ monomeric units.

The γ form contains a sucession of structural layers in such a manner that they determine a cubic close-packing of the chlorine atoms. The unit cell of this form belongs to the hexagonal system and contains six monomeric TiCl$_3$ units. The δ form can be obtained hy prolonged grinding of the etiher the α or β forms of TiCl$_3$ and the X-ray powder spectrum shows an essentially disordered structure. The α, γ, δ forms are colored violet, while the β form is brown. These TiCl$_3$s can have the simple composition (one Ti per three Cl) or a more complex structure whereby a second metal is cocrystallized as an alloy in the TiCl$_3$ crystal. The particular method of reduction determines both the composition and crystalline modification. Table 3.11 summarizes the synthesis of the most important TiCl3's that have been reported in Ziegler-Natta literature. Much credit must go to the Natta school, which did so much to elucidate the structures of the various modifications, their catalytic activity, and stereoregulating ability.

The early investigations of propylene polymerizations of the Natta school were done with the pure α-TiCl$_3$ modification combined with AlEt$_3$. The α-TiCl$_3$ was synthesized by reduction of TiCl$_4$ with H$_2$ at elevated temperatures (500 to 800 $^\circ$C) [87]. TiCl$_4$ can be reduced with aluminum powder at lower temperature (about 250 $^\circ$C) : the formed TiCl$_3$ also has the α-crystal structure but , in

addition, contains Al cations in the crystal lattice. In later polymerization studies, these α-TiCl$_3$ were replaced by more active modifications, nakely the γ and δ forms. The γ modification is formed by heating the β modification (at 100 to 200 $^\circ$C) ; the higher the temperature, the shorter is the time required for the transformation. For a β modification containing one Al per three Ti, the transformation takes only several hours at about 140 $^\circ$C.

The β modification (free of Al) is synthesized by decomposition of CH$_3$TiCl$_3$, but this form does not form a highly active and highly stereo-reugulating catalyst for polymerization of propylene to isotactic polypropylene. The γ modification derived from it also has a low activity. The preferred compositions contains Al cations, and they are synthesized by reducing one TiCl$_4$ with about 1/3 AlEt$_3$, one AlET$_2$Cl, or 1-2 Al$_2$Et$_3$Cl$_3$.

The δ crystalline modification is synthesized by prolonged grinding of the αand γ forms. Because the γ TiCl$_3$ (containing AlCl$_3$) is already highly active. it is not practical to transform it to the δ form . On the other hand, the activity of the αTiCl$_3$ form (containing AlCl$_3$) is much improved by transforming it to the δ form. Figure 3.16 summarizes the observed transformations of the various crystalline modifications.

Based on the utilization of the α, γ and δ forms in the polymerizations of propylene (with AlEt$_2$X), the following results were obtained :

(1) The different crystalline forms of violet TiCl$_3$ give rise to catalyst system whose stereospecificity depends almost entirely on the organometalic compound used for the catalyst preparation and does not depend upon the particular modification of violet TiCl$_3$.

(2) The stereospecificity of the catalyst systems examined on the organoaluminum compounds.

(3) For the catalytic systems prepared from violet TiCl$_3$ with or without aluminum, and for the organometallic compounds examined, the following scale of stereospecificity was established.
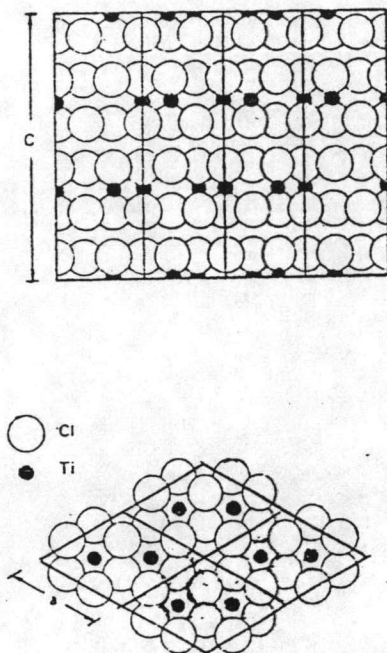
$$AlEt_2I > AlEt_2Br > BeEt_2 > AlEt_2Cl > AlEt_3$$
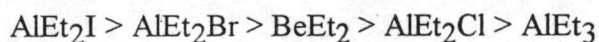
Figure 3.14 Crystalline structures of α(violet) titanium trichloride
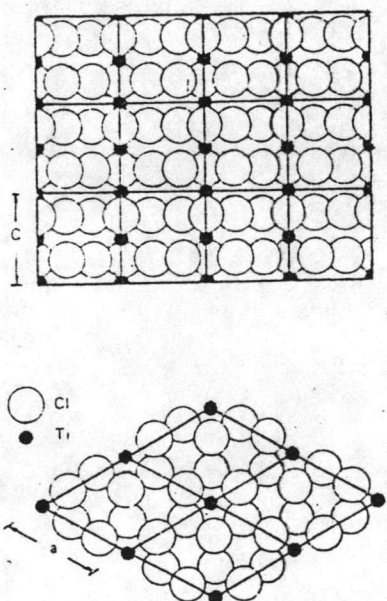

Figure 3.15 Crystalline structure of β(brown) titanium trichloride

Table 3.11 Preparation of the α, β, γ, δ and Crystalline Modifications of Titanium Trichlorides ($TiCl_3$ and $TiCl_3.xAlCl_3$ Types)

Expt. no.	Preparation	Crystalline form	Composition
1a.	$TiCl_4+H_2$ at high temp.(800)	α	$TiCl_3$
b.	$TiCl_4+Al$ at 100°-200°C in aromatic solvent	α	$TiCl_3 .0.33 AlCl_3$
c.	$\beta TiCl_3$ heated to 300°-400°C	α	$TiCl_3$
d.	$3TiCl_4+Al+0.5AlCl_3>190°C$ (no solvent)	α	$TiCl_3 .0.5 AlCl_3$
e.	$2TiCl_4+Mg+2AlCl_3>200°C$ (no solvent)	α	$2TiCl_3.0.5 MgCl_2.AlCl_3$
f.	$9TiCl_4+Ti+2Al>200°C$ (no solvent)	α	$TiCl_3 .0.33 AlCl_3$
2a.	CH_3TiCl_3 heated $> 25°C$ ($AlMe_2Cl$ or $AlMe_3+TiCl_4 \rightarrow CH_3TiCl_3$)	β	$TiCl_3$
b.	$TiCl_4+H_2$ exposed to silent electric discharge at low temp. or to γ radiation	β	$TiCl_3$
c.	$TiCl_4+AlR_3$ or AlR_2Cl or $AlEt_2Cl < 25°C$	β	$TiCl_3 .\alpha AlCl_3$
d.	$TiCl_4+$activated Al below 100°C (e.g. in benzene at 80°C)	β	$TiCl_3 .0.33 AlCl_3$
e.	$TiCl_4+Al,AlCl_3$:aromatic solvent and ether treatment	β	$TiCl_3$ (98%)
3a.	$\beta TiCl_3$ $\Delta120°-200$ °C,up to several hours	γ	$TiCl_3$
b.	$TiCl_3 xAlCl_3$,$\Delta120°-200$ °C,up to several hours	γ	$TiCl_3 AlCl_3$
c.	$TiCl_4 + Al + AlCl_3$, inert sovent	γ	$TiCl_3 xAlCl_3$
d.	$TiCl_4 + Al$ at 160 °C in 9:1 $C_{10}H_{12}$ / xylene, solvent	γ	$TiCl_3 0.33 AlCl_3$
4a	$\alpha TiCl_3$ mechanical grinding, 25 °C	δ	$TiCl_3$
b.	$TiCl_3 xAlCl_3$, mechanicla grinding, 25 °C	δ	$TiCl_3 xAlCl_3$
c.	$\alpha TiCl_3 + AlCl_3$, mechanical grinding	δ	$TiCl_3 xAlCl_3$

$$\alpha TiCl_3 \xleftarrow{\substack{heat \\ 300\ ^\circ C\text{-}400\ ^\circ C}} \beta TiCl_3$$

heat 100 °C | prolonged grinding (B) | heat 25 °C-200 °C
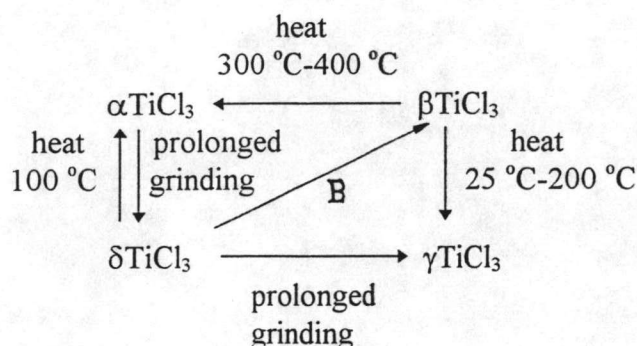
$$\delta TiCl_3 \xrightarrow{} \gamma TiCl_3$$

prolonged grinding

Figure 3.16 Crystal-crystal transformations which occur most readily with the alloyed compositions $TiCl_3.xAlCl_3$ (A) The rate of transformation increases with increasing temperatures (B) The possibility of converting $\delta\ TiCl_3$ to $TiCl_3$ and $\alpha TiCl_3$ was suggested by Wilchinsky, Looney, and Tornqvist [88].

Besides the effect of structural modifications of $TiCl_3$ upon catalyst activity,it was found that the state of subdivision of the $TiCl_3$ could affect the polymerization rate. Thus, in the polymerization of propylene using α-$TiCl_3$ and $AlEt_3$, if the $TiCl_3$ is in the form of relatively large crystals (linear dimension about 10 μ), the activity increases during an adjustment period that is related to the cleavage of the largfe crystals. However, with finely dispersed $TiCl_3$, the opposite effect occurs, the small crystals tend to coalesce. When finely dispersed $TiCl_3$ was used and was subsequently stabilized by heating, the polymerization rate reached a constant value in a few minutes.

The $AlCl_3$ is present as a solid solution in the crystal lattice. An isomorphous substitution for titanium atoms of aluminum occurs during the formation of the crystal. The aluminum cation is not essential for the titanium trichloride to be active, but when present the activity of titanium trichloride is significantly increased. For example, the $TiCl_3.xAlCl_3$ composition (x = 0.33) are about two to seven times more active than any of the aluminum-free TiCl3 compounds [89]. Highest activites have been reported when x is about 0.33 in these alloy composition.

3.11.2 Nature of the Catalyst Surface

It was previously indicated that stereoregularity tended to increase at the expense of the polymerization rate, the form of β-TiCl$_3$ favored the latter, while the α, γ and δ forms favored the former characteristic. Thus it is not surprising that Stearn [92] found the rate of propylene polymerization to be a function of the degree of disorder (amorphicity) in the TiCl$_3$ crystal, the disorder being obtained from the integrated intensity of the X-ray diffraction band due to the [003] reflection.

Minsker and Bykhovskii have discussed the role of surface electron defects in Ziegler-Type catalyst systems. The catalystic activity of certain heterogeneous catalysts was attributed to the presence of electrons which are localized in defects of the "color center" type. In order to account for the inclusion of antibonding molecular orbitals of monomers in the transition state, monomer reactivity parameters such as energy of singlet-triplet excitation, the energy of the first unoccupied molecular orbital, electron affinity, etc., must be considered.

A possible reason for the existance of "impurity" crystals containing "color centers" involves the chemisorption of the metal alkyl onto the ionic lattice of TiCl$_3$. Thus an aluminium atom in AlR$_3$ could interact with the surface chlorine anions due to the greater affinity of the aluminmium atom for chlorine than for the carbon atom in the alkyl group. In this manner, an ionic lattice of the Ziegler-type catalyst can contain (AlR$_2$)$^+$ cation formed from AlR$_3$ in the field of the surface chlorine anion. Hence, and "impurity" crystal results with an anionic vacancy near which may be found an R- carbanion. When there are defects present prior to chemisorption effects, chemisorption of the metal alkyl should be facilitated and polymerization should occur preferentially at such sites.

Electron defects may be caused by mechanical grinding of ionic crystal compare the formation of δ-type TiCl$_3$, electrolysis, irradiation with electron, X-rays etc. When an impurity crystal is formed with a highly distorted lattice due to the inclusion of AlR$_3$, AlR$_2$Cl, etc., stereocontrol may be impaired. Reaction involving the anionic vacancy may occur when an anion near the vacancy shares an electron with an olefinic monomer. This results in formation of a σ-bond between a carbon atom of the anion and a carbon atom of the monomer. In this process, the anion remains near an anionic defect. In the course of shaping an electron, the barrier to internal rotation about the double bond of the monomer is lowered and allows the monomer to orient in a field of low excitation, e.g., the

repulsive field of the surface atoms of the lattice. In this manner, an isotactic configuration may result.

The electron defect theory is supported by various experimental findings. Thus, it can be used to explain why the addition of only a very small amount of AlEt$_3$ to crystalline TiCl$_3$ leads to stereospecific polymerization of propylene whereas "pure" TiCl$_3$ obtained from the reduction of TiCl$_4$ with H$_2$ is inactive. When the reduction occurs, the formation of electron defects may occur due to the ionization of hydrogen atoms and the subsequent chemisorption of H$^+$ on the ionic lattice to form F centers. Since the ionization potential of the hydrogen atom (13.5 eV.) is much higher than that of the alkali metals (3-5 e.V.), the formation of electron defects of this type is less probable, which may result in inactive "pure" TiCl$_3$. However, on reduction of TiCl$_4$ using metal alkyls, etc., electron defects can result. The theory can also explain the effect of additives, e'g', amines, on polymerization rate. The additive can coordinate about the electron to a higher atomic or molecular level. Thus, the ionization potential of the coordinated active center is decreased, which facilitates electron sharing and increases the rate of polymerization. The rate increase may also be attributed to the ability of the additive to coordinate with TiCl$_3$ which facilitates the breakdown of the crystals and leads to move active centers as well as to displacement of an unpaired electron of TiCl$_3$ to a higher level.

3.11.3 Effects of Aging and Pretreatment

Catalyst age may be defined as the time interval between mixing of the catalyst components and the introduction of the monomer into the system. Its influence on catalyst activity is still rather controversial.

It was found that aging effect on the polymerization may depend upon the R group in AlR$_3$. When R = Et, aging time did not exert any appreciable effect on polymerization rate of ethylene in the presence of TiCl$_4$ at a particular temperature. However, a marked effect could be observed with catalyst prepared with AlEt$_2$Cl and AlEtCl$_2$. Thus, aging effects became more pronounced as the chlorine content of the aluminum alkyl increased. The apparent effect was to slow down the formation of active centers. Thus, in the polymerization with AlEt$_2$Cl-TiCl$_4$ at a ratio of 1.0, by increasing the aging time, a relatively large increase in polymerization rate occurred (Figure 3.17). With AlEtCl$_2$-TiCl$_4$, reaction occurred after 2 hr. of aging but remained at a low rate even after 23 hr. of aging.

It was previously indicated that aging did not appear to affect the activity of the catalyst system, $AlEt_3$-$TiCl_4$, at a particular temperature. However, Kodama and co-workers[91] found that the activity of such a catalyst decreased considerably with time at 60°C. The catalyst was maintained at a definite temperature for a definite time interval and was then used as a polymerization catalyst. The results are shown in Figure 3.18. Although catalyst activity did not change much at 30 ^{o}C for up to 4 hr., it decrease rapidly at 60°C. Since polymerization rates even at 30 ^{o}C decrease with reaction time for a "normal" polymerization, it becomes difficult to definitely attribute the rates decrease to catalyst deactivation.

Hoeg and Liebman [92] studied the effects of aging on the polymerization of propylene, using $TiCl_3$ and $AlEt_3$ or $Al(i$-$C_4H_9)_3$. They found that these catalysts were thermally unstable. Thus, when they were stored above 120 ^{o}C., lower overall polymerization rates were obtained. However, when propylene was added immediately after AlR_3 addition, polymerization rate increased with temperature. At high temperatures, catalyst activity was found to decrease as the Al/Ti ratio increased. This was attributed to the formation of lower valence states of titanium which presumably are less stable and less efficient as catalysis at the high temperatures employed.

It has also been found that washing the Ziegler-type catalyst may greatly affect its catalytic activity[93]. Thus, if a Ziegler catalyst is prepared in the usual manner in octane using $TiCl_4$-$Al(i$-$C_4H_9)_3$, the resulting dark brown slurry is an active catalyst for ethylene polymerization. When the solid phase is separated from the liquid phase and both are tested for activity, only the solid phase shows activity when it is redispersed in octane. However, when the solid phase was washed on a filter with octane until no more soluble organometallic compounds were removed, it exhibited very little activity when redispersed in octane. The addition of fresh aluminum alkyl in octane to the inactive dispersed slurry restored its activity to almost the magnitude that it possessed prior to washing.
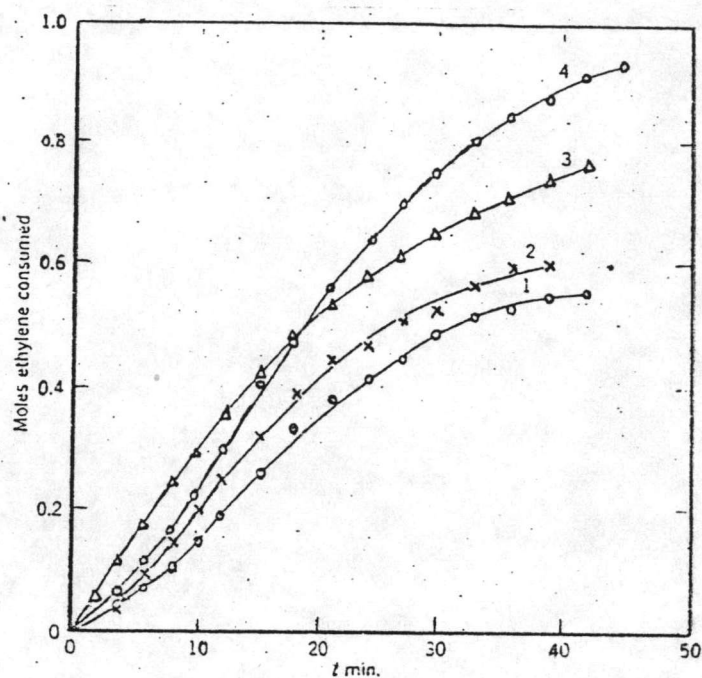
Figure 3.17 Effect of aging of the Et_2AlCl-$TiCl_4$ catalyst system on the rate of ethylene polymerization
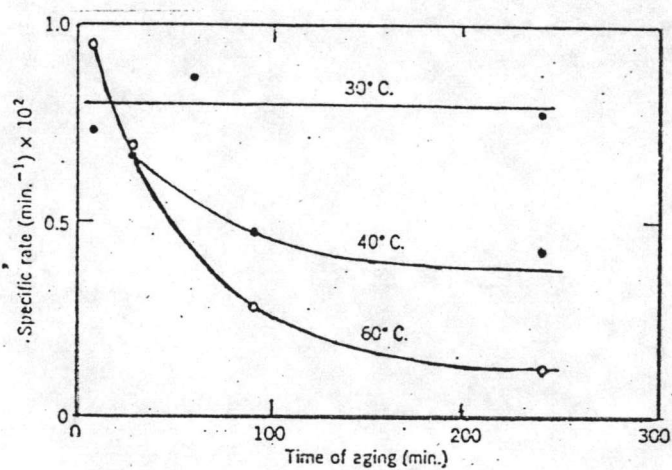
Aging time : (1) 2 min., (2) 5 min., (3) 10 min., (4) 25 min.

Figure 3.18 Effect of aging on the specific rate of propylene polymerization (Catalyst system : $AlEt_3$-$TiCl_4$; polymerization were carried out at aging temperatures)
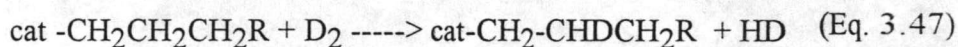
3.11.4 Effects of Oxidation State

Schindler[94] used deuterium gas (D_2) as a probe to differentiate types of titanium center in $AlEt_3$-$TiCl_4$ and $AlEt_2Cl$-$TiCl_4$ systems. His work aimed at showing that both trivalent and tetravalent titanium centers are active when used for polymerizing ethylene. The polyethylene that was formed under these conditions had CH_2D, CHD, and CD_2 groups present according to infrared spectroscopie measurements. The CH_2D group was readily explained by a transfer reaction, as show in Eq. (3.45)

$$cat\text{ -}CH_2CH_2CH_2R + D_2 \text{ -----> } cat\text{-}D + DCH_2\text{-}CH_2CH_2R \quad \text{(Eq. 3.46)}$$
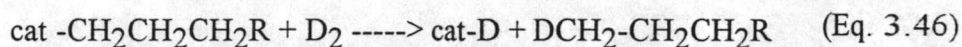
The CHD and CD_2 groups move explained by an exchange reaction involving D_2 and the lable β-hydrogen, as show in Eq. 3.46.

$$cat\text{ -}CH_2CH_2CH_2R + D_2 \text{ -----> } cat\text{-}CH_2\text{-}CHDCH_2R + HD \quad \text{(Eq. 3.47)}$$

Schindler concluded that the active center that produced these results contained Ti(IV). This assessment was based on the earlier findings of Bestain and Clauss[95] that the β-hydrogen of a polyethylene chain which is attached a Ti(IV) center is very liable. A couble exchange would give CD_2.

Beerman and Bestian [8] proposed that an alkylated tetravalent titanium in the presence of some solid $TiCl_3$ was the active catalyst when ethylene was polymerized with partially decomposed CH3TiCl3. The latter was not active unless some of the CH_3TiCl_3 decomposed to form solid $TiCl_3$.

Some workers have argued that the oxygen oxidizes inactive lower valent state sites to active tetravent sites. Others have proposed that the activating effect of oxygen is actually due to the greater ability of tetravalent titaniums to be realkylated incontrast to lower valent sites [94].

If the titanium trichloride and the aluminum alkyl are mixed and used for polymerization under mild conditions, the oxidation state of the Ti remains III. Favoring such conditions are low mixing and polymerization temperatures, low concentration of metal alkyl, and use of a metal alkyl that has a low reducing capacity, such as $AlEt_2Cl$ or $AlEtCl_2$. Partial reduction to divalent state occurs when the catalyst components are mixed and used for polymerization at higher

temperature, as well as when the metal alkyl is used at a high concentration or if a strongly reducing alkyl is used, including $AlEt_3$ or $ZnEt_2$.

3.11.5 Effects of Catalyst Ratio

Catalyst ratio can also influence polymerization rate, polymer yield, and stereoregularity. From Figure 3.19 it can be seen that as the ratio increases, the specific rate reaches a maximum value and then decrease with increasing ratio for the system $AlEt_3$-$TiCl_4$-propylene[133]. Such behavior appear to be typical for Ziegler-Natta systems which are based on $TiCl_4$.

When α - olefin are polymerized by Ziegler-Natta Catalysts based on $TiCl_3$ we may say that , in general, as the catalyst ratio increases, the rate of polymerization increases to a maximum value and then levels off as the ratio is increased further. This may not apply to diolefins.
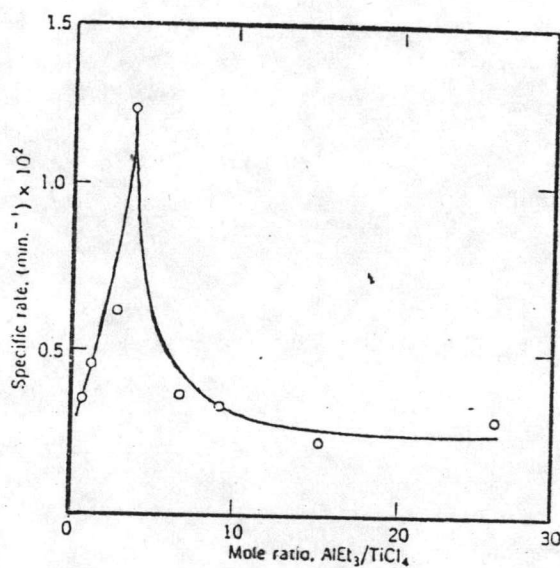

Figure 3.19 Effect of catalyst ratio, $AlEt_3$/$TiCl_4$, on the specific rate in propylene polymerization.

Tacticity of polymer may depend upon the catalyst ratio. In the case of styrene polymerization with a catalyst based on $TiCl_4$ and $AlEt_3$[97] it was found that as the ratio was increased up to a value of about 3, ataticity decreased and tacticity increased; for ratios above this value the drgree of tacticity decreased again. The low tacticity of the polymers obtained at lower catalyst ratios was attributed to the presence of unreacted $TiCl_4$. At higher ratios (above 3), excess unreacted AlR_3, which lowers yield and tactictiy, may be present. Such an effect may be explained if it is assumed that the excess AlR_3 competes with monomer for adsorption on the active catalyst surface and also begins to cover the surface to a relatively large extent, thereby decreasing stereospecific activity.

Catalyst activity of systems involving aluminum alkyl derivatives has been found to drecrease in the order.

$$AlR_3 > AlR_2X > AlRX_2 > AlX_3$$
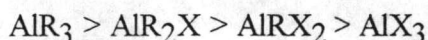
Obviously, reaction temperature and reaction time will affect the quantities of products obtained in the interaction of catalyst components.

3.11.6 Effects of Catalyst Components

The catalyst components used will also affect the structures of poly-olefins. These influences can be summarized in the following way:

(1) The presence of lyophilic groups on either the titanium derivatives or the alkylaluminum compoumds decrease the quantity of isotactic polymer obtained in -olefin polymerization.

(2) As the size of the alkyl group in trialkylaluminum compound increases from ethyl to hexyl, the stereospecificity of polymer decreases. This effect has been attributed to the formation of more colloidal catalyst system with increasing size of the alkyls group. In general , Ziegler-Natta catalysts containing large particles yield crystalline polymers whereas with finely dispersed catalyst more amorphous products result.

(3) The nature of the halogen attached to the titanium is also of some influence on the stereospecificity.

(4) The most stereospecific catalysts are those which involve a metal having a very small diameter, e.g., aluminium, beryllium, lithium. A strong

influence on molecular weight of polymer exciting from the type of metal organic compound are also found.

3.11.7 Miscellaneous Factors

Order of mixing the monomer and the catalyst components was found by some authors to exert a great influence on catalyst activity in Ziegler-Natta polymerizations. Orzechowski [98] found for the polymerization of ethylene using $TiCl_4$-$Al(i$-$Bu)_3$ that the order of addition of catalyst compoonents must be $TiCl_4$ followed by $AlEt_3$, otherwise less active catalysis resulted. Also activity was enhanced when the second component was injected slowly. If the rate of component interaction were slow with respect to both rates of stirring and addition, the order of addition should not affect catalyst properties. Thus, when $TiCl_4$ is injected into AlR_3 the latter is in excess and this may favor the formation of products such as AlR_2Cl and $TiCl_2$ as well as $TiCl_3$. However, when AlR_3 is injected into $TiCl_4$ the excess of the latter may favor the formation of products such as $AlCl_3$ as well as $TiCl_3$. The latter, in the absence of excess reducing agent will resist further reduction to the Ti(II) state. The net effect is to increase catalyst activity, as judged by the polymer yield.

It is understandable that different catalytic mixtures will be formed when the components $AlEt_3$ (or $AlEt_2Cl$) and $TiCl_4$ are mixed and used under different conditions. The nature of the catalyst changes with polymerization time. Some workers stabilized the preparations by a prepolymerization aging at ambient or higher temperaturees, but this produced only a partial improvement.

3.12 Modification

The efficiency of Ziegler-Natta polymerization can be improved by several methods. These methods appear to provide catalyst improvement in exposing and isolating the maximum amount of transition metal compound either in a solid support or an additional substance. This section attempts to describe some of the breakthroughs in catalyst technology and understanding which resulted in the revolutionary process improvements.

3.12.1 First generation catalysts

The first commercial catalysts were natural extensions of Ziegler and Natta's pioneering work. Typically $TiCl_4$ was reduced at low temperatures with triethylaluminum in a hydrocarbon diluent, resulting in the precipitaiton of $TiCl3.1/3$ $AlCl_3$. Although this material, being β- $TiCl_3$, can provide the polymerization of ethylene, it is not suitable for isotactic polypropylene manufacture. Hence, the slurry was slowly heated to 160-200 ^oC for several hours to effect the phase transformation to the purple γ-$TiCl_3$ form necessary for the final catalyst. The efficiency and selectivity of these first catalyst were so poor that improvements were sought by :

(1) Ball-milling the catalyst, which enhance catalyst efficiency somewhat by generating smaller $TiCl_3$ crystallites and hence more active centers.

(2) The use of electron donors to increase stereoselectivity. By the late 1960's electron donors such as ethers, esters and amines were frequently used as a "third component" in propylene polymerization. These lewis base can increase catalyst activity by disproportionating the catalyst poison, ethyl aluminum dichloride(EADC) which being present via reaction product of cocatalyst.

3.12.2 Second generation catalysts

An understanding of the nature of $TiCl_3$ catalyst increased, it became clear that their performance was limited by two constraints :

(1) The presence of cocrystallized $AlCl_3$ which led to formation of the catalyst poison DEAC.

(2) The large size of catalyst ($TiCl_3$) crystallites, resulting in a low proportion of active Ti sites.

The improvement in catalyst performance was realized by, prior to polymerization, removing much of the cocrystallized $AlCl_3$. Via washing with a suitable solvent such as toluene or ether. However, it became apparent that, at the elevated temperatures (160-200 ^oc) used in converting brown β-$TiCl3$ to purple γ, δ-$TiCl_3$.

The breakthrough came in the early 1970's and resulted in a second generation of catalysts with significantly improved performance (by a factor of four

or more, at given stereoselectivity). Although simplified preparative routes have been developed, second generation catalyst manufacture essentially involves the reduction of $TiCl_4$ with alkylaluminum at low temperature to afford brown β-$TiCl_3.xAlCl_3$ (similarly to first generation catalysts) followed by ether extraction of $AlCl_3$ and heat treatment at 60-100°c in the presence of excess $TiCl_4$, resulting in the final purple δ-$TiCl_3$ catalyst. The action of $TiCl_4$ is twofold-removal of excess ether ($TiCl_4$ being a stronger Lewis acid than $TiCl_3$) and , most importantly, catalysis of the transformation of β-$TiCl_3$ into stereoselective δ-$TiCl_3$ at low temperature (<100°C).

3.12.3 Third generation catalysts

"Supported Ziegler-Natta" catalyst is preferential designation of a $TiCl_4$ catalyst on a specially prepared $MgCl_2$ support. In order to combine a high polymer yield with good stereoselectivity a complexed cocatlayst is used, most frequently a mixture of trialkylaluminum and an electron donor such as ethyl benzoate or ethyl toluate. Although not applied commercially until about 1980, the development of supported catalysts has paralleled that of conventional $TiCl_3$ catalysts for more than 25 years $MgCl_2$ is the optimum support for $TiCl_4$, since it has the same layer lattice as the stereoselective purple γ-$TiCl_3$ catalysts and since Mg^{2+} (0.066 nm) and Ti^{4+} (0.068 nm) are very similar in ionic radius. In the layer lattice structure (single layer) of $MgCl_2$, magnesium ions fill all the octahedral holes between the two chloride layers (giving the observed $MgCl_2$ stoichiometry). In the case of $MgCl2$ there exists no chain lattice analog of β-$TiCl_3$ this fact greatly simplifies the problem of generating small catalyst crystallites.

There is a wide variety of routes to prepare such high activity supported catalysts, as is reflected by the abundant patent literature (>400 patent applications in the last 10 years). One commonly described method involves a ball-milling procedure which usually takes the form of a two-step manufacturing procedure. First anhydrous $MgCl_2$ is ball-milled with an electron donor such as ethyl benzoate to afford the catalyst support. Similar to $TiCl_3$ as described above, crystalline $MgCl_2$ exists in the form of agglomerates of small primary crystallites; the ball-milling procedure serves to reduce greatly the size of these primary crystallites. The second step of the catalyst preparation involves bringing $TiCl_4$ on to the ball-milled support.

Three different types of Mg ions can be distinguished on the surface of a MgCl$_2$ crystal (Figure 3.20)

Type 1 on the lateral faces: single-vacancy Mg ions having an effective charge of 0 e;

Type 2 on the corners: single-vacancy Mg ions having an effective charge of -2/3 e;

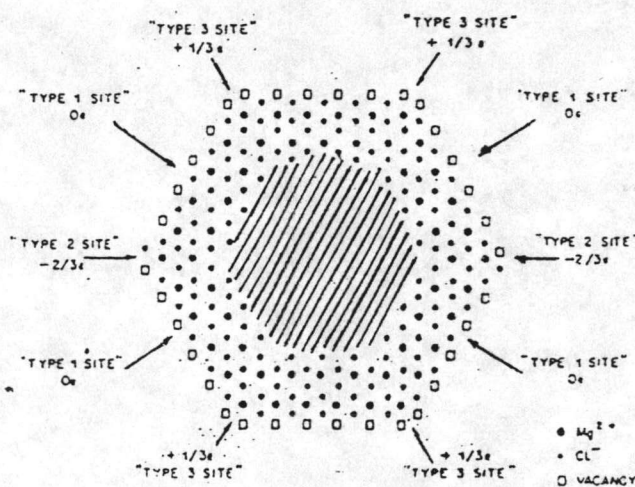Type 3 on the corners: double-vacancy Mg ions having an effective charge of +1/3 e.

Figure 3.20 Surface structure and sites of hexagonal MgCl$_2$ crystallites

Using various analytical techniques, the catalytically active TiCl$_4$ is determined to bound to the doublevacancy (Type 3) Mg ions higher stability of MgCl$_2$-supported TiCl$_4$ towards reduction allows the use of trialkyl aluminum of the catalysts with very activity. Just as with TiCl$_3$ catalysts, "third components" (particularly aromatic esters such as p-ethyl anisate) are used to control stereoselectively.

3.12.4 Disadvantages

Although the highly stereospecific performance and high catalytic activity can be contributed by the various modification mentioned above, many undesirable consequence can be contaminated.

According to inorganic support containing, the polymer is not too useful for clear film application. Low catalyst residue content is also important since the catalyst is made with chlorine containing materials such as titanium, aluminium , and magnesium chlorides. High residual chlorine values in a polymer resin can cause pitting and corrosion on the metal surface of the molding devices. Chlorine residue of the order of >= 200 ppm are not commercially useful.

Although the electron donnor used as an in gradient of the catalyst or used in the preparation of the catalyst can provide the polymerization efficiency of the Ziegler-Natta catalysts, the consequence arising from this is an offensive odor and coloration in the resulting polymer. Another trouble is that some types of the electron donor consume the organoaluminum compound, the amount of the organoaluminum compound as a cocatalyst should be very large. To avoid any disadvantage both in operation and equipment of after-treating the polymer. the further improvements of Ziegler-Natta catalyst have been prospected.

In the matter of molecular weight distribution (MWD), it is very important for the qualitative control of the polymer products as well as for their optimal utilization. Regulation of MWD and achievement of the relevant process know-how are still being investigated by various researchers. Unfortunately, knowledge on this matter is rather poor and we are very far from a deep comprehension of the synthesis parameters governing molecular weight distribution.

In the years to come further catalyst improvements can be expected, not only in terms of catalyst performance but also in the direction of product "tailoring" to generate new or improved grades of polyolefins. These new breakthroughs will only be made possible by increasing the understanding of the organometallic chemistry involved, particularly with respect to the in reactions taking place between the catalyst and cocatalyst.

3.13 PROCESS

3.13.1 Slurry Processes for Polypropylene

Several modifications of slurry processes have developed and current processes are in general much simpler and cheaper to operate than earlier versions. These processes are either operatted batchwise or with continuous-flow operation. In addition, some slurry processes use a hydrocarbon solvent, but others do not. In all cases , however, a slurry is present in the polymerization reactors, and solid particles that are primarily polypropylene are suspended in the liquid phase. The solid particles also contain finely dispersed catalyst particles and adsorbed overtrapped propylene, comonomers,and solvent (if one is used). The liquid phase contains primarily solvent and propylene. If a solvent is not used, the reaction is controlled so that only part of the propylene is polymerized, and the polymerization can be characterized as bulk (or mass polymerization. The unreacted propylene then acts as the liquid to suspend the polypropylene particles. In all slurry processes, some low-molecular-weight and amorphous polypropylenes are dissolved in the liquid phase.

Process steps that have been or still are employed in polypropylene manufactureinclude the following:

1. Catalyst preparation that may in some cases be completed in situ in a polymerization vessel.

2. Polymerization of propylene and possible comonomers to produce the product slurry. This step is obviously always the most important one.

3. Recovery and recycling of the unreacted propylene.

4. Recovery and recylng of the solvent if one is used.

5. Destruction and separation of the catalyst or its residue from the final polymer.

6. Removal of amorphous (or atactic) and low-molecular-weight polypropylene form the solid polypropylene particles formed in the reaction vessel. The objective frequently is to produce polypropylene that is almost completely crystalline (and isotactic).

7. Finishing operations for the polypropylene product, such as drying, blending additives,and extrusion and pelletizing.

If a catalyst could be developed which resulted in essentially complete isotacticity in the product and which was extremely active, steps 5 and 6 could be

simplified, if not eliminated, with a significant savings in operating expenses. Although no such catalyst has apparently been developed, chances of doing so in the next few years seem good. By proper choice of posttreatment techniques, steps 5 and 6 are often accomplished simultaneously. Furthermore, step 4 is also eliminated if no solvent is used and liquid propylene is used instead as the suspending liquid.

Although of lesser importance than the slurry processes just described, solution processes are used for the production of both homopolymers and copolymers of propylene. In these processses, the polymer produced is dissolved in the liquid phase of the reactor. Detail have been reported[ ] of two different versions of a process and catalyst system developed by Eastman Kodak Co. In the first verson, a paraffinic hydrocarbon boiling in the range of about 180 to 200 °C is employed. The second version really empolys a bulk- (or mass-) polymerization technique, and propylene is the "solvent" for polypropylene. This process, however ,differs from the bulk process in which polypropylene was not dissolved.

In order to dissolve polypropylene, fairly high temperatures (160 to 250°C) are required, and hence higher pressures are needed in order to dissolve appreciable amounts of propylene in the liquid phase and to obtain high rates of polymerization.

Several examples of the large-scale production of polypropylene are reported by Hagemeyer and Edwards (20). When a paraffinic hydrocarbon was used as the solvent, two 500-gal autoclaves connected in series were used as reactors. Propylene, solvent, and catalyst were continuously added to the first reactor, and additional propylene was introduced (probably through a sparging device) to the second reactor. The reaction mixture was maintained at about 160 to 173°C and 1,000 lb/in^2 gage (about 70 atm). The exit solution from the second reactor contained (in example reported) 30 to 38 percent dissolved polypropylene, 18 to 23 percent absorbed propylene, and the remainder solvent. It is estimated that residence times of about 1 h are employed in the reactors, and hence approximately 2,000 lb/h of polypropylene are produced in these two autoclaves.

Polypropylenes with melt flow rates of 1.56 to 2.42 produced by this solution process had much higher impact strengths and lower brittleness temperatures than a conventional polypropylene with a melt flow rate of 4.62 produced by a slurry process. The solution-type polypropylene was 88 percent crystalline based on extraction with hexane.
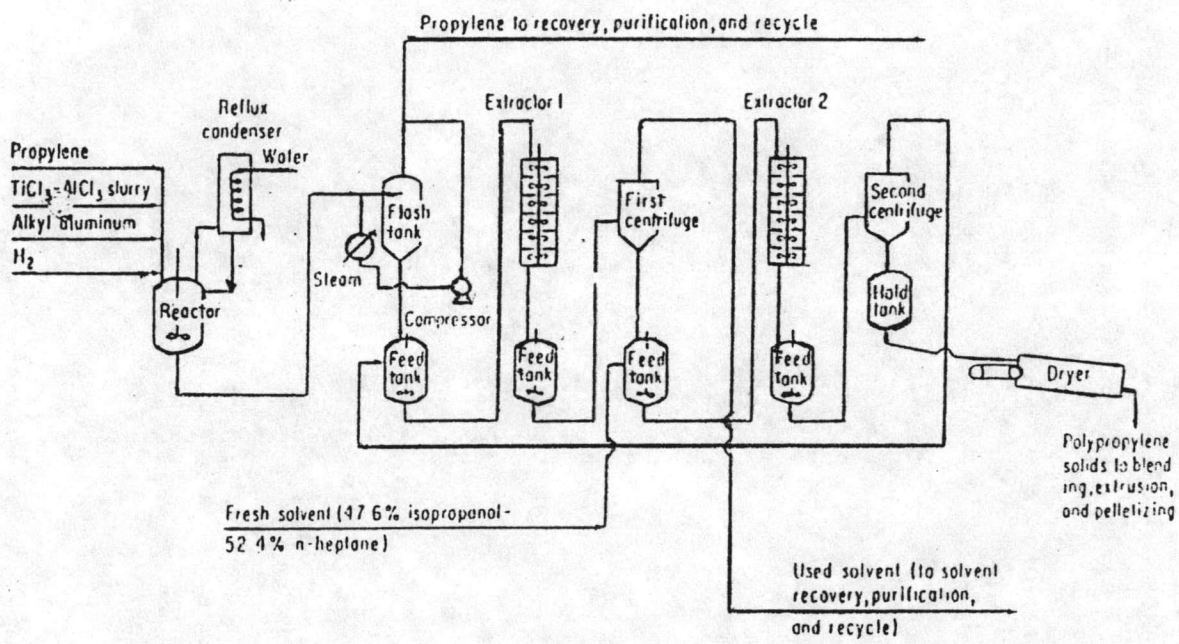
Figure 3.21   Flowsheet of Rexall polypropylene process, in which reactor contains a slurry of solid polypropylene suspended in liquid polypropylene.

Solution Processes for Polypropylene

The solution processed, however, have significantly higher polymerization costs than slurry processes, for several reasons. First, higher-pressure reaction vessels are required. Second, and most important, recovery of polypropylene from a solution is rather expensive compared with recovery steps for a slurry process. Futher, in a slurry process, there is the opportunity, during the catalyst-removal steps, to remove at least most of the atactic polypropylene. In a solution process, atactic polypropylene can be removed only if additional (and expensive) extraction steps are incorporated in the overall process scheme.

3.13.2 Gas-Phase Polymerization of Propylene

Propylene can be polymerized by gas-phase processes [   ], and at leastone such process is now being operated commercially [   ] . BASF is producing 24,000 metric tons/year of polypropylene at their Rheinische Olefinwerke in Wesseling, West Germany. This polypropylene is quite different from conventional polypropylenes. It has a relatively low level of crystallinity since about 25 to 28 pecent of it is heptane-soluble but its impact strength is much better than that of conventional polyprolene.

The dry liquid propylene is them continuously added to the bottom of the polymerization reactor, and a modified Ziegler-Natta catalyst is added at the top. A mixture of solid particles and upflowing propylene gas is present inside the reactor. The solid particles are primarily polypropylene containing finely divided catalyst.The solid catalyst fragments as the propylene polymerizes and as the size of the polypropylene granules (or powder) grows.

To be economically competitive, gas-phase processes require a catalyst for which essentially no separation steps are required after the polymerization reactor. Separation steps for catalyst residuesor atactic (or noncrystalline) polypropylene would increase the operatin costs excessively. Although such separation steps are not practiced in the BASF process, it should be emphasized that BASF makes a rather unconventional polypropylene. As yet a suitable catalyst has apparently not been developed for production of conventional polypropylenes by gas-phase processes, i.e., for production of polypropylene with only low concentrations of atactic polypropylene. There is hope, however, that such catalyst can be found in the near future. If such a catalyst is developed, gas-phase processes will probably find large-scale commercial applications.