Evolution of Ziegler-Natta Catalysts for Polymerization of Olefins

Akhoury Sudhir Kumar Sinha and Umaprasana Ojha

Abstract This chapter provides a brief account of the discovery and gradual evolution of Ziegler-Natta catalysts for polymerization of various olefins, α-olefins, and functional olefins. The structure of first and second generation catalysts is introduced, and the different mechanisms proposed by the scientists for the polymerization of ethylene using this catalyst is discussed. Subsequently, the control of branching and mechanism to produce stereospecific poly-α-olefins is elaborated. Development of catalysts for synthesis of stereo-controlled polyolefins is discussed along with methods to determine the stereospecificity of the polymers. The evolution of metallocene-based Ziegler-Natta catalysts and the mechanism of polymerization based on these catalysts are briefed. The following section discusses about the catalyst compositions useful for polymerization of functional olefin monomers and their copolymerization with propylene. Development of catalyst compositions based on Pd, Ni, Cu, and Fe is discussed, and subsequent polymerization mechanism is included. A series of catalysts synthesized using vanadium and various chelated ligands are discussed in context of their catalytic activity and the structure of polymer formed. The last chapter unveils some of the recent advances in these categories of catalysts and future scope of the catalyst.

Keywords Ziegler-Natta catalysts · Polymerization mechanism · Stereospecific polyolefins · Tridentate ligands · Vanadium-based complexes · Polyolefins synthesis

1 Introduction

Polyethylene (PE) was a serendipitous invention by Reginald O. Gibson and Eric W. Fawcett of Imperial Chemical Industries (ICI) in 1933. The above two organic chemists, while performing a reaction between ethylene and benzaldehyde in an

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Table 1 Mechanical and thermal properties of HDPE, MDPE, LLDPE, and LDPE

Properties	HDPE	MDPE	LLDPE	LDPE
UTS (psi)	2200–6530	1810–5080	1150–6600	1500–2600
Young's modulus (10^5 psi)	0.90–2.10	1.16	0.20–2.27	0.28–0.75
Ultimate elongation (%)	3–1900	50–1100	8–1100	100–850
Melting point (°C)	130–140	126–128	75–128	108–121
Flexural modulus (10^5 psi)	0.7–7.0	0.86–1.74	0.02–1.10	0.22–3.20
Density (g/cm^3)	0.93–1.27	0.93–1.05	0.87–0.96	0.91–0.95

The properties were collected from matweb.com
UTS ultimate tensile strength

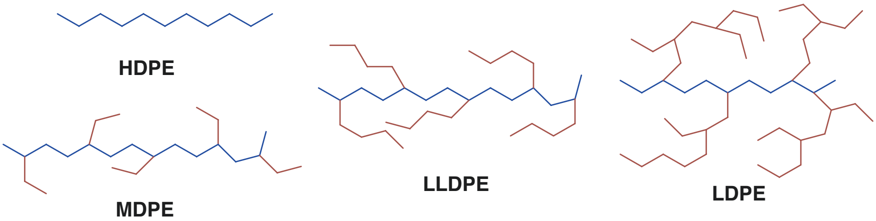


Fig. 1 Schematic representation of the polymer chains of high-density PE (HDPE), medium-density PE (MDPE), linear LDPE (LLDPE), and LDPE

autoclave, observed formation of a white, waxy, and light substance. Apparently, a drop in pressure due to an inadvertent leak and presence of trace amount of oxygen facilitated the polymerization and formation of this plastic material. This revolutionary plastic substance was later termed as PE. Soon PE found its first commercial application, and a patent on this polymer was filed by ICI in 1936. In 1944, the real commercial implementation of PE commenced. Both DuPont and Bakelite Corporation obtained the license from ICI to start large-scale commercial production of PE. PE possessing excellent commercial value owing to its moisture and chemical and electrical resistance is one of the major petrochemical products. Currently, PE is synthesized in a large scale in several countries all over the world with around 90 million metric tons of production per year. The C2 and C3 olefin side products emanating from the fluid catalytic cracking units have promoted the large-scale production of PE.

However, the PE synthesized under free radical condition was low-density PE (LDPE) and exhibited inferior mechanical properties with low tensile strength and Young's modulus along with low melting point and low crystallinity (Table 1). In presence of a free radical initiator such as peroxides and azobisisobutyronitrile (AIBN) and under high pressure and temperature conditions, inter- and intramolecular chain transfer to polymer chain resulted in long- and short-chain branching (Fig. 1). Occurrence of these chain transfer reactions increased the polydispersity index (PDI), broadened the molecular weight distribution, and lowered the packing efficiency and density of the samples. As a result, the mechanical properties of LDPE were compromised to certain extend.

2 Zeigler-Natta Catalyst

The commercial viability of PE took a revolutionary leap in 1953 after the momentous invention of a versatile organometallic catalyst for polymerization of ethylene by Karl Waldemar Ziegler of the Kaiser Wilhelm Institute and Erhard Holzkamp. Ziegler utilized a binary mixture of transition metal halides of group IV and metal alkyls of group I to III, typically $TiCl_4$ and $AlEt_3$ to polymerize ethylene under normal pressure and room temperature conditions [1]. The procedure was able to minimize the branching and produced high-density polyethylene (HDPE). Soon after this invention, Giulio Natta and coworkers further demonstrated the versatility of this catalyst and trivalent titanium chloride-based system to polymerize different α-olefins such as propylene and butylene to produce stereoregular isotactic polymers [2]. This path-breaking invention led to development of commercial plastics and elastomers, and living cationic, anionic, and radical polymerizations evolved with time, expanding the research and development on synthetic high polymers. The income earned from his patents ensured financial independence and further expansion of the Institute of which he was the Director.

Since 1955, the scientific literature exploded especially with several thousands of reports on utilization of these catalysts for polymerization of a range of olefins and dienes and further modification of the catalyst to improve the versatility and efficiency. This chemistry associated with the name of Karl Ziegler is considered as one of the "historical landmarks in chemistry," and in recognition to their efforts, both Professor K. Ziegler and G. Natta were honored with the prestigious Nobel Prize in Chemistry in 1963. In general, though the number of variations in transition and alkyl metals is large, the number of useful combinations for efficient catalysis is limited. Titanium and vanadium have so far displayed excellent activity, and zirconium, hafnium, and tungsten have shown promise for future development. Similarly, in case of alkyl metals, aluminum have been outstanding and utilized in a number of catalyst compositions followed by magnesium and zinc in selective cases. The versatility of this Ziegler-Natta catalyst is ascertained to the number of monomers these catalyst systems can efficiently polymerize and the number of different products those can be obtained from each monomer.

2.1 Mechanism of Polymerization

Several mechanistic pathways are proposed in the literature towards the polymerization of olefins in presence of Ziegler-Natta catalyst. Most of the reports agree to one general aspect of the polymerization, i.e., the polymerization occurs through insertion of olefin monomer between the metal atom and one of the alkyl groups of the organometallic compound. However, some disagreement still exists regarding the nature of active center, i.e., the growing polymer chain is attached to the transition metal or the non-transition metal.

2.2 *Mechanism Based on Bimetallic Complex*

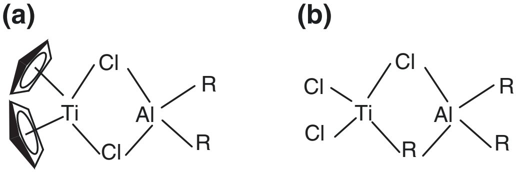
Natta and Mazzanti proposed a bimetallic mechanism while studying the ethylene polymerization using a soluble complex of titanium chloride and aluminum alkyl (Fig. 2a) [3]. Similarly, Furukawa and Tsuruta also supported the bimetallic mechanism, and the complex of AlR_3-$TiCl_3$ was proposed to be responsible for polymerization (Fig. 2b) [4]. In a later stage, several other researchers including Huggins, Boor, and Patat supported the above bimetallic mechanism.

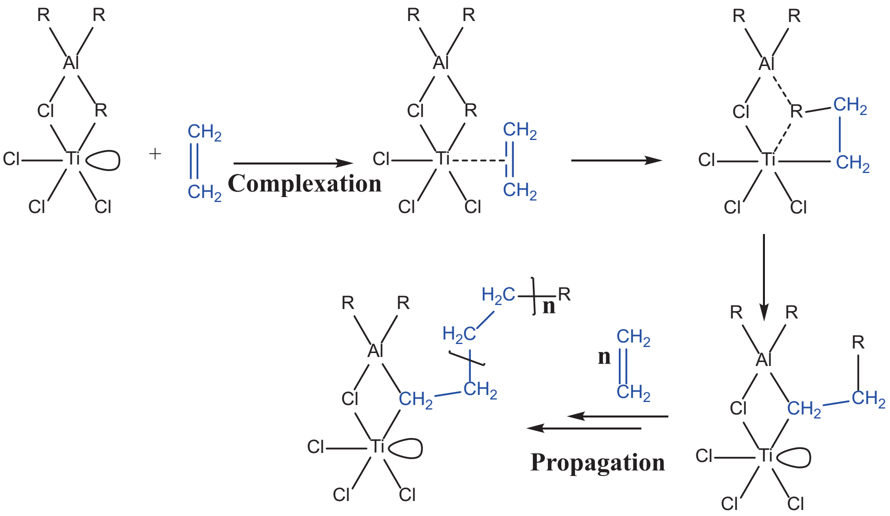
As per the mechanism proposed by Rodriguez et al., since the Ziegler-Natta polymerization is stereospecific, a bimetallic complex is involved as shown in Scheme 1 [5]. The vacant t_{2g} orbital on the Ti atom is forming a π-complex with the olefin monomer as a part of the initiation step. Subsequently, insertion of the olefin occurs between Ti-C bond and simultaneous rupture of Al-C bond. The alkyl group migrates to the olefin carbon, and the CH_2 of olefin replaces the alkyl group originally placed between Ti and Al. The active center is restored now after insertion of one olefin moiety. The propagation occurs via repetition of the above olefin insertion steps, and polyolefin possessing the alkyl group at the chain end is obtained after the polymerization.

2.3 *Mechanism Based on Monometallic Complex*

Cossee proposed that a monometallic complex is involved in the polymerization and the active center is an alkylated Ti-ion [6]. As per the detailed study by Arlman and Cossee, a penta-coordinated alkyl titanium complex is formed by exchange reaction of titanium chloride with alkyl aluminum (Scheme 2). The vacant site on the alkyl titanium complex formed π-complex with the olefin monomer. Subsequently, insertion of olefin occurred between the Ti and alkyl group, and the vacant site on Ti surface was restored for addition of next monomer. Involvement of alkyl titanium

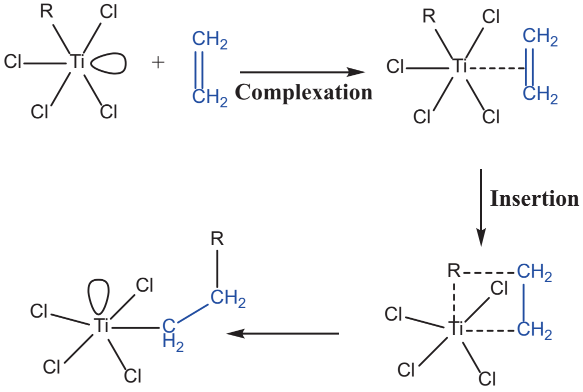
Fig. 2 Bimetallic complexes used by (**a**) Natta et al. and (**b**) proposed by Furukawa et al. responsible for polymerization of olefin





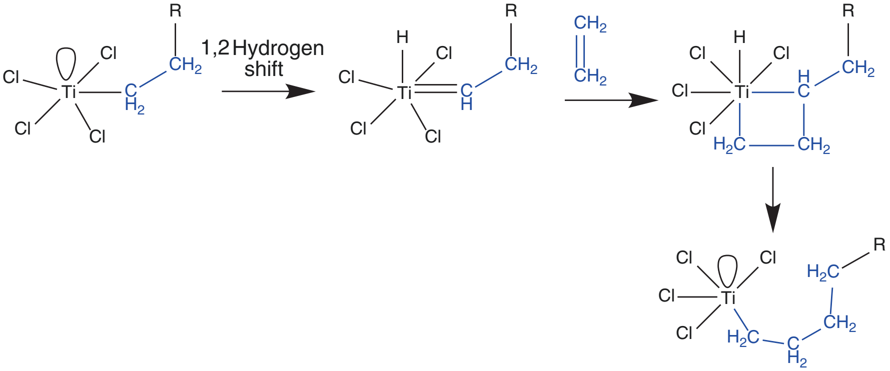
Scheme 1 Olefin polymerization mechanism based on bimetallic complex by Rodriguez

Scheme 2 The monometallic mechanism for Ziegler-Natta polymerization proposed by Arlman and Cossee



complex in the polymerization mechanism was already supported by Ludlum and Ziegler [7, 8]. The role of alkyl aluminum is primarily to serve as the alkylating agent. Cossee further reasoned that for formation of π-complex between metal and olefin, the d orbital of metal atom must be sufficiently large to efficiently overlap with the anti-bonding orbital of the olefin. This particular case is suitable with metal possessing low effective nuclear charge. In fact, Natta had already proposed that the metals with ionization potential less than 7 eV are suitable for such π-complex formation.

The most intriguing aspect of the mechanism is carbon-carbon bond formation. In this regard, Rooney and Green proposed that the mechanism involves 1,2-hydrogen shift from the α-carbon to the metal surface followed by the formation of metallocyclobutane (Scheme 3) [9]. As per this mechanism, the metathesis involving



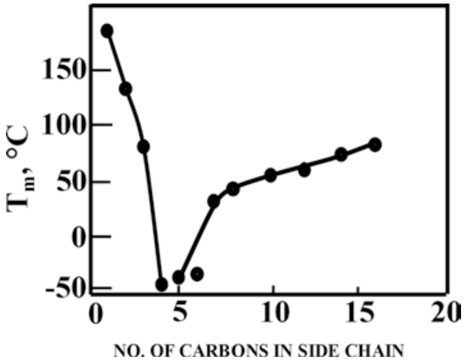
Scheme 3 The polymerization mechanism based on hydrogen shift proposed by Rooney and Green

metallocyclobutane and metal-olefin-carbene interconversion guided the polymerization. The kinetics of the polymerization was anticipated to be strongly dependent on the isotopic effect if the hydrogel shift was part of the mechanism. However, Grubbs soon reported that the isotopic effect on the polymerization is absent or negligible that tilted the mechanism in favor of Arlman and Cossee theory [10]. Corradini et al. further studied the Cossee model via computation of non-bonded interactions at the catalyst surface. They proposed that the olefin coordinates in an inward position to minimize the steric hindrance on the catalyst surface. This strongly restricts the orientation of the first carbon-carbon bond, which may explain the stereospecificity of the polymer chain [11]. This allowed the synthesis of stereoregular polyhydrocarbons (Scheme 3).

3 Synthesis of Stereospecific Polyolefins

Stereoselective poly-α-olefins are especially important, since the thermal and mechanical properties of isotactic poly-α-olefins are strongly dependent on the number of carbons in the side chain of the monomer. For example, the melting temperature (T_m) of the poly-α-olefins decreases from 176 to −50 °C by changing the number of carbons in side chain from one to six (Fig. 3). The T_m further increases to 80 °C on increasing the number of carbons in the side chain to 17 [12]. Over the period of time since discovery of Ziegler-Natta catalyst, the catalyst composition was varied to produce stereoselective polyolefins. A substantial research was devoted to achieve technological advances with the existing catalyst system. In 1970, matrix-supported catalyst system was reported in which the titanium chloride was supported on crystalline $MgCl_2$ matrix. Soon, research on development of homogeneous catalyst gained momentum. Especially, the homogeneous catalyst systems were suitable to synthesize polyolefins with syndiotactic polypropylene.

Fig. 3 Melting points of isotactic poly-α-olefins

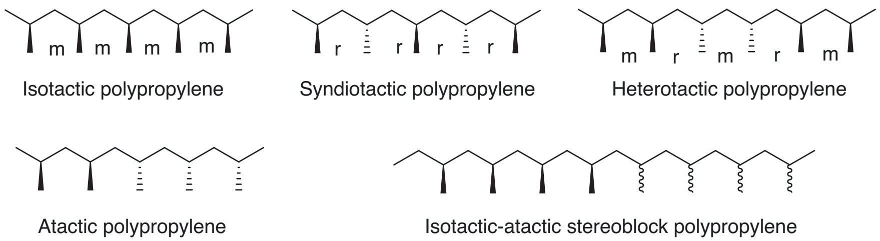


Bis(cyclopentadienyl)titanium chloride and trialkyl aluminum-based catalyst compositions were studied as possible homogeneous system for polymerization of ethylene.

The catalytic activity of these systems was dependent on the chloride content of these catalysts [13]. Interestingly, Vollmer and coworkers showed that in presence of trace amount of water, these catalyst systems even in absence of chloride content efficiently polymerized ethylene [14]. Furthermore, the molecular weight of resulting polymer was dependent on the polymerization temperature. For example, a tri(cyclopentadienyl)zirconium- and trialkylaluminum-based catalyst system effectively polymerized ethylene, and the molecular weight increased from 40,000 to 1.5×10^6 g/mol on decreasing the temperature from 90 to 50 °C. Controlled synthesis of methylalumoxanes from trialkylaluminum in presence of water was proposed to be the key factor in improving the efficiency of these systems [15]. Soon the potential of Cp_2MX_2-AlR_3 systems as efficient polymerization catalyst was realized, and systems based on other group 4 metals such as Zr or Hf were studied. However, the polymerization of propylene in presence of bis(cyclopentadienyl)M(IV), where M is Ti or Zr, and methylalumoxanes produced atactic structures (Fig. 4) [16].

Catalysts and conditions were optimized to produce isotactic and syndiotactic polypropylene. Ewen synthesized a polypropylene with mmmmmrmmmmmr stereo sequence using bis(cyclopentadienyl)bis(phenyl)titanium catalyst system (Fig. 5) [17]. Two successive methyl groups on same plane were assigned as a meso (m)-diad, whereas two successive methyl groups in opposite plane are assigned as racemic (r)-diad.

Nuclear magnetic resonance (NMR) spectroscopy was utilized to estimate the population of stereospecific segments and corresponding configuration in the polypropylene samples. The relative intensities of pentads mostly followed a Bernoullian statistical distribution of a chain-end controlled stereospecific polymerization (Table 2). The ^{13}C NMR spectroscopic data revealed that under low temperature conditions, the steric factor predominated the stereochemistry of monomer insertion reaction. The ^{13}C resonances in the range of 19–23 ppm were studied to understand the presence and population isotactic (m) type sequences in the polypropylene chains. The m sequences were observed at higher chemical shift region (~21.5 ppm).



Isotactic polypropylene

Syndiotactic polypropylene

Heterotactic polypropylene

Atactic polypropylene

Isotactic-atactic stereoblock polypropylene

Fig. 4 Schematic representation of stereo-controlled polypropylene chain

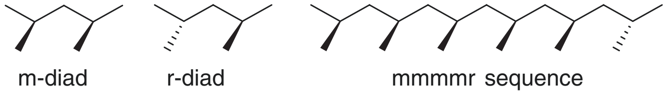


Fig. 5 The schematic representation of m-diad, r-diad, and mmmm pentad configuration of polypropylene chain segment

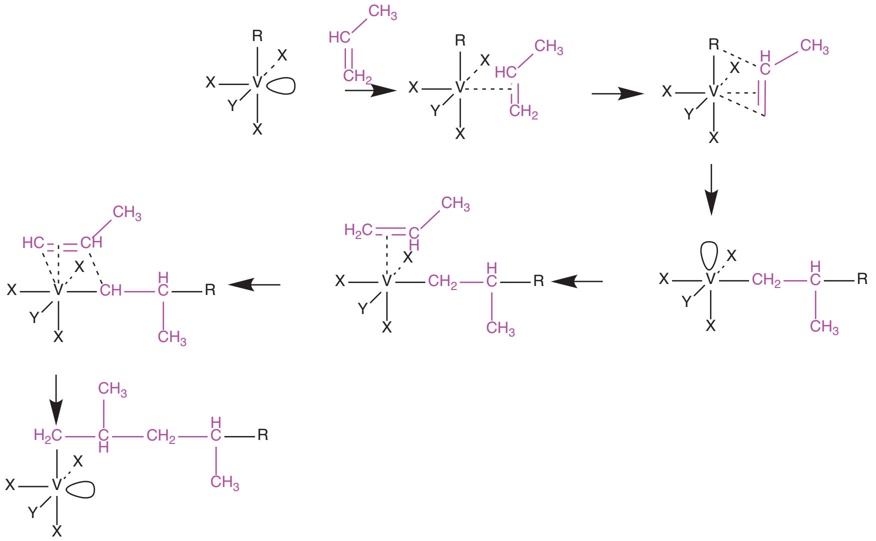
Table 2 The Bernoullian probability distribution of stereochemical sequences, especially diads and pentads in polypropylene chains [20]

Sequence	m	r	mm	mr	rr	mmmm	mmmr	rmmr	mmrr	mrmm	rmrm	rrrr	rrrm	mrrm
Bernoullian	P	(1-P)	P^2	2P(1-P)	$(1-P)^2$	P^4	$2P^3(1-P)$	$2P^2(1-P)^2$	$2P^3(1-P)$	$P^2(1-P)^2$	$2P^2(1-P)^2$	$2P(1-P)^3$	$P^2(1-P)^2$	$(1-P)^4$

Similarly, the methylene (CH_2) carbons resonated in between 44 and 46 ppm [18]. The polymerization data revealed that the polypropylenes synthesized at low temperature (−45 °C) conditions possessed mmmm pentads with small amounts of mmmr and mmrm pentads [17]. The stereoregularity of the polymer increased up to 85% on decreasing the polymerization temperature to −60 °C. Similarly, the $VC1_4$-$Al(C_2H_5)_2Cl$ catalyst system produced syndiotactic polypropylene with similar stereoregularity [19]. Furthermore, the syndio-regulating ability is reinforced in presence of cyclohexene, oxygen, or *tert*-butyl perbenzoate.

The bulkiness of R group in alkyl aluminum halide and the nature of halide (when halide is chloride only) controlled the syndio-regularity of polymer. The reaction conditions such as low temperature (−40 °C) and shorter polymerization period favored the above stereospecificity of polypropylene. Addition of anisole as donor with donor:V ratio as one under low conversion scenario and a non-polar solvent like heptane complemented the yield of syndiotactic polypropylene. Boor et al. proposed the mechanism to be coordination-anionic type with an alkylated vanadium species acting as the active site. The initiation occurred with complexation of propylene to the V empty orbital (Scheme 4).

Subsequently, the CH_2 and CH of the monomer formed bond with V and R, respectively, through a concerted four-membered ring pathway. During the course



Scheme 4 Mechanism for the formation of syndiotactic polypropylene in presence of $VC1_4$-$Al(C_2H_5)_2Cl$ catalyst system

of polymerization, development of partial +ve charge on CH and −ve charge on CH_2 moieties of the monomer guided the cis opening and head-to-tail arrangement of the monomers in the polymer chain. The opposite complexation mode is less preferable since this required opposite polarization of the charge in the double bond. The formation of isotactic chains was only possible if free rotation of V-R bond was possible in the active site. However, such rotation was restricted due to the presence of halide further favoring the above complexation mode. This also suggested that the size of central atom and nature of ligand have significant roles to play to obtain syndio-specific chains as rotational barrier is key to the above stereospecificity.

4 Catalysts for Isotactic and Syndiotactic Poly-α-olefins

Both isotactic and syndiotactic poly-α-olefins possessed contrasting properties and were important from the prospective of application. A comparative tensile properties data of the polypropylenes with different tacticity is summarized in Table 3. The syndiotactic polypropylene is soluble in ether and hydrocarbon solvents unlike the isotactic ones. The T_m of syndiotactic polypropylene is ~40 °C lower compared to that of the isotactic analog possessing similar crystallinity. Similarly, the isotactic polypropylene has a higher unit cell density (0.94 g/cm^3) and much higher heat of fusion (2350 cal/unit) compared to that of the syndiotactic polypropylene (unit cell density = 0.90 g/cm^3, heat of fusion = 450 cal/unit). Owing to this, specialized catalyst compositions to synthesize stereospecific polypropylenes rich with isotactic or

Table 3 Properties of isotactic, syndiotactic, and atactic polypropylene (PP) [22]

Properties	PP	Isotactic PP	Syndiotactic PP
UTS (MPa)	40	600	330
Elongation at break (%)	100	130	230
Young's modulus (GPa)	1.9	20.0	3.0
Density (g/cm^3)	0.89–0.92	0.91–0.94	–
Melting point (°C)	–	171	130

syndiotactic chains are desirable. Typically, the isotactic and syndiotactic character is defined by the amount of m and r-diads present in the polymer. In an isotactic polypropylene, the extent of m-diad can be more than 99%, whereas the amount of r-diad in a syndiotactic polypropylene can extend up to 85% [21].

Collette et al. developed a series of metal oxide-supported group IVB metal-based R_4M (M = Ti, Zr, and Hf; R = benzyl, neophyl, and neopentyl) type catalyst systems [23]. These R_4M catalysts supported on Al_2O_3 exhibited high efficiency with 600 g of polymer/nM R_4M, and the resulting polymers were of high molecular weight. The isotactic content in the polypropylene reached up to 70%. The stereoregulation was strongly dependent on the M:Al_2O_3 ratio and the amount of M on the surface. Presence of H_2 further improved the yield but compromised the crystallinity. The Table 4 below summarizes the yield, molecular weight, and thermal properties of the polypropylene obtained based on different catalyst. The T_m (147 °C) of the polypropylene obtained using Al_2O_3-supported catalyst was observed closed to that of the $TiCl_4/MgCl_2/AlEt_3$-based system (T_m = 159 °C). However, the polydispersity indices (M_w/M_n) of the former (8.0) were compared to that of the $TiCl_4/MgCl_2$-based system (5.6). Presence of H_2 marginally increased the T_m of the samples to 151.8 °C, though the M_w/M_n further increased to 10.0. The major concern in these solid supported systems was the yield. The value (47.7 g/mmol of metal) was much inferior compared to that of the $TiCl_4/MgCl_2$-based system (2680 g/mmol of metal). Importantly, the molecular weight (M_n = 75,500 g/mol) of the polypropylene based on solid-supported catalyst was much higher compared to that of the $TiCl_4/MgCl_2$-based system (22,400 g/mol) suggesting the polymerization is faster in case of the former.

Ewen et al. showed that catalyst systems may be developed by selecting suitable ligands to predominantly synthesize either isotactic or syndiotactic polypropylene. A C_2-symmetric metallocene catalyst based on indene produced isotactic polypropylene (Fig. 6a). A stereorigid C_5-symmetric prochiral catalyst based on cyclopentene and fluorene produced syndiotactic polymer predominantly (Fig. 6b). The mechanism of syndiotactic polymer formation was attributed to the chain migratory insertion of monomer as shown in Scheme 5. The two accessible sites on the catalytic sites are for the growing chain and the incoming monomer. If the growing chain shifts between these two sites at each monomer addition, then a syndiotactic polypropylene is the preferred product. However, several authors also hypothesized that the steric repulsion between the methyl group of the complexed monomer and last unit of the growing chain guided the above stereoselectivity of the polymer [24].

Table 4 Properties of polypropylene obtained using different catalyst compositions [23]

Catalyst	Yield[a]	Fraction	%	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	$M_n \times 10^3$	$M_w \times 10^3$
TNZ-Al_2O_3	47.7	Total	100	10.2	−10.1	147.1	13.1	75.5	600
		Ether Sol.	28.2	3.81	−8.0	52.0	1.6	80.8	604
		Hept. Sol.	17.9	4.78	−7.8	130.2	27.7	39.3	934
		Hept. Insol.	50.0	15.3	−7.4	147.7	49.0	455	2626
TNZ/Al_2O_3 + H_2 (5 psi)	92.7	Total	100	4.08	−11.5	151.8	5.0	34	370
		Ether Sol.	49.0	2.54	−8.8	53.0	1.8	22.3	261
		Hept. Sol.	33.0	3.28	−10.1	137.0	29.2	22	478
		Hept. Insol.	24.0	8.04	−7.5	149.9	68.7	108	3460
$MgCl_2$/$TiCl_4$/$AlEt_3$	2680	Total	100	2.11	−394	159.6	62.5	22.4	128
		Ether Sol.	21.0	0.82	−3.6	nd	nd	19.1	66.8
		Hept. Sol.	19.3	0.78	−1.6	140.1	63.0	28	110
		Hept. Insol.	53.0	3.45	nd	166.3	102.0	160	531
$MgCl_2$/$TiCl_4$/$AlEt_3$ + H_2 (5 psi)	2140	Total	100	0.53	−9.8	159.0	78.2	12.1	42.3
		Ether Sol.	26.6	0.31	−10.4	Nd	nd	6.7	16.5
		Hept. Sol.	24.5	0.28	−1.8	156.4	63.5	10	26.7
		Hept. Insol.	45.7	0.83	nd	161.3	105.0	26.8	110

The polymerization was carried out in heptane at 60–65 °C for 1 h

TNZ tetraneophylzirconium

[a] g/mmol of metal

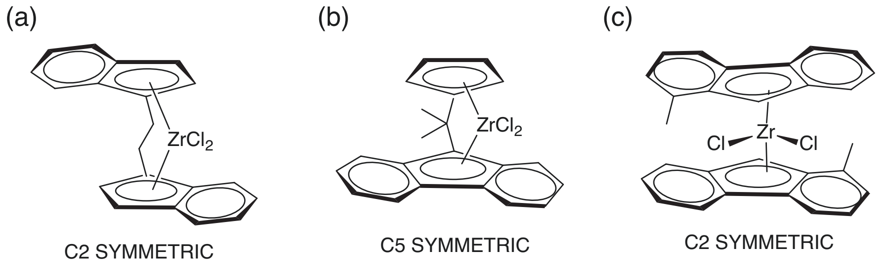
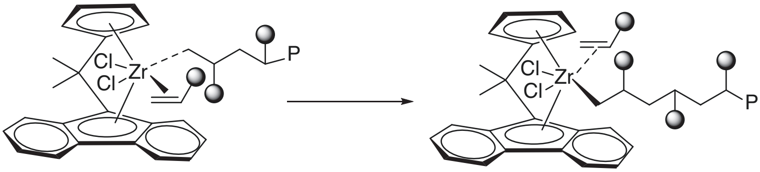


Fig. 6 Structures of the stereorigid (**a**) C_2-symmetric, (**b**) C_5-symmetric, and (**c**) unbridged C_2-symmetric metallocene catalysts



Scheme 5 The mechanism for syndiotactic propagation of the polymer chain as proposed by Ewen et al.

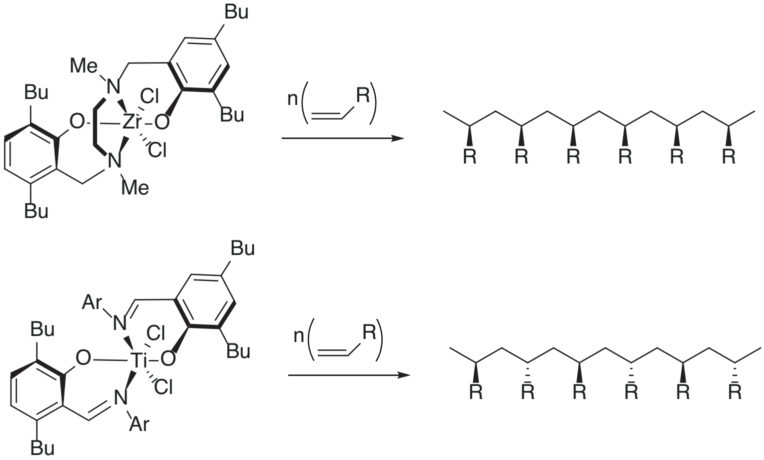
Table 5 Properties of polypropylene synthesized using metallocene-based catalyst

Properties	Polypropylene from metallocene-based catalyst	Polypropylene from first-generation metallocene-based catalyst
Melting point (°C)	161	162
M_w/M_n	2.5	5.8
Tensile strength (N/mm^2)	1620	1190
Hardness	86	76

These metallocene-based systems revolutionized the synthesis of stereo-controlled poly-α-olefin using a homogenous catalyst. These catalyst systems rendered a better control over the distribution of molecular weight and ratio of monomers in a copolymer. The properties of polypropylene synthesized using metallocene-based catalyst system also improved compared to that of first-generation Ziegler-Natta catalyst system (Table 5) [25, 26].

The geometry around the metal center of these metallocene catalysts were presumed to be pseudotetrahedral. Subsequently, catalyst based on octahedral complex possessing C_2 symmetry and a N-C-C-N bridge was developed that produced isotactic poly-α-olefin with mmmm-pentad content up to 80% [27]. Interestingly, when the bridging from the above catalyst was removed, the catalyst efficiently produced syndiotactic poly-α-olefin with rrrr-pentad amount of 96%. A close analysis of the origin of stereoregularity in these systems revealed that the insertion of monomer is a key parameter in regulating the stereospecificity of the resulting polymer. The monomer either inserts in primary (the primary carbon is bonded to the metal atom) or secondary (the secondary carbon is bonded to the metal center) manner (Scheme 6). The primary insertion is dominant in the bridged systems, whereas the secondary insertion mostly occurs in case of the unbridged catalysts with octahedral geometry similar to that of the homogeneous vanadium-based catalyst.

Presence of chiral active species in catalyst is necessary to guide the stereoselection between two monomer enantiofaces during insertion in the following two ways. Firstly, the coordination of ligands to the metals is responsible for the chirality of the active sites. For example, the relative orientation of the two bidentate ligands in the catalysts shown in Fig. 8 is interchangeable if the bridging is absent. However, in presence of bridged chemical linkage, the system becomes stereorigid, and no interchange is possible. Secondly, the chirality of the tertiary carbon of the last inserted



Scheme 6 Bridged and unbridged C_2-symmetric octahedral catalysts for poly-α-olefin synthesis

monomer in the growing polymer chain regulates the incoming enantioface of the incoming monomer. If the insertion of prochiral monomer is guided by the chirality of the catalytic site, then the phenomena is termed as chiral-site stereocontrol. If the chirality is guided by the conformation of the last inserted monomer, then chain-end stereocontrol occurs. The chain-end stereocontrol follows the Bernoullian statistics of the r or m stereochemical sequences, whereas non-Bernoullian statistics originates from chiral-site stereocontrol. A stereo mistake if occurs during polymerization gets propagated for chain-end stereocontrol, whereas the same stereo mistake under chiral-site stereocontrol remains isolated having little effect on the site chirality.

These metallocene catalysts are especially useful for polymerization of cyclic olefins (cyclopentene, norbornene, and substituted compounds) and synthesis of copolymers (Fig. 7). The copolymer of ethylene and propylene exhibits elastomeric properties. At low temperature, selectivity of monomer addition is observed with metallocene catalysts leading to block copolymer. More specifically, the polymerization catalyzed by hafnocenes polymerizes propene first followed by ethylene. The polymerization of cyclopentene follows 1,3-enchainment, whereas the polymerization of norbornene proceeds through 1,2-addition. The processing temperature of polycyclic olefins may be decreased by copolymerizing with ethylene.

5 Catalysts for Polymerization of Functional Olefins

Polymers based on functionalizable olefin monomer such as methyl acrylate, vinyl ethers, acrylamides, and acrylic acid are important from commercial point of view with potential applications in the areas of anticorrosive coatings, food packaging, and antioxidants. These functional monomers were initially polymerized under free

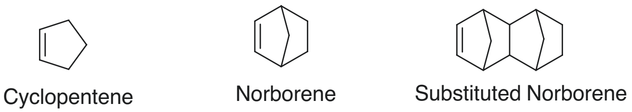


Fig. 7 Cyclic olefin monomers polymerizable using metallocene catalyst

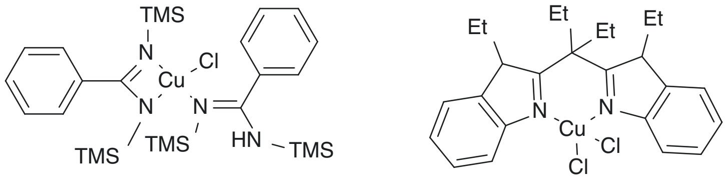
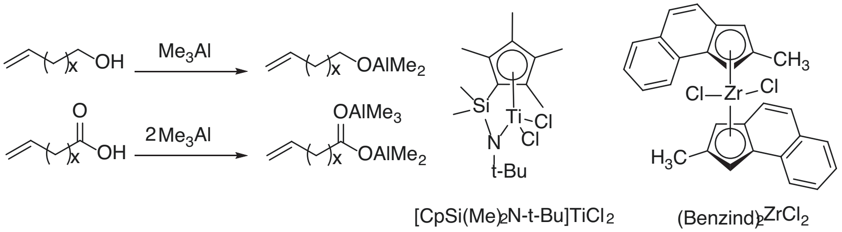


Fig. 8 Copper(II)-based catalyst systems for polymerization of olefins



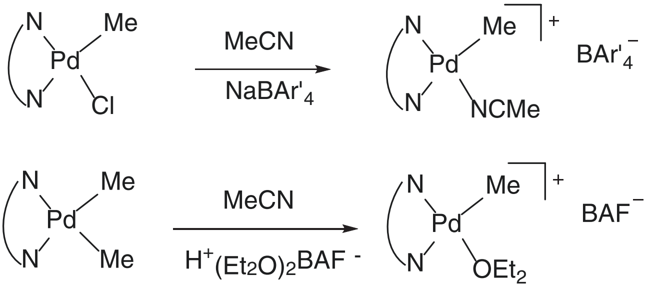
Scheme 7 Protection of functional groups with trimethyl aluminum and the catalysts used for polymerization of functional monomers

radical conditions. Recently, efforts were made to develop Ziegler-Natta catalysts for polymerization of these monomers. However, early transition metals were oxophilic, and the titanium-, zirconium-, and chromium-based catalysts were easily poisoned by these functional olefins possessing oxygen-based functional groups. Late transition metals though less oxophilic possess weak catalytic efficiency and produce oligomers of olefin. One of the approaches to circumvent this issue was to protect the polar functional group present in the monomer during polymerization. For examples, trimethyl aluminum was utilized to protect the –OH and –COOH functional groups present in the polymerizable monomer [28]. The protected monomers were polymerized using zirconium-based metallocene catalysts $(Benzind)_2ZrCl_2$, $[CpSi(Me)_2N\text{-}t\text{-}Bu]TiCl_2$, and $[Et(Ind)_2]ZrCl_2$ (Scheme 7). The resulting polymers displayed molecular weight up to 197,000 g/mol with polydispersity index value in the range of 1.9–2.9. The functionalities were regenerated by hydrolyzing the protected groups, subsequent to the polymerization. However, during copolymerization, the incorporation of these protected monomers was lower compared to that of the ethylene and propylene due to the steric factor associated with these systems. Less than ~10 mol% of the functional monomers were incorporated in a copolymerization of ethylene and 10-undecen-1-oic acid.

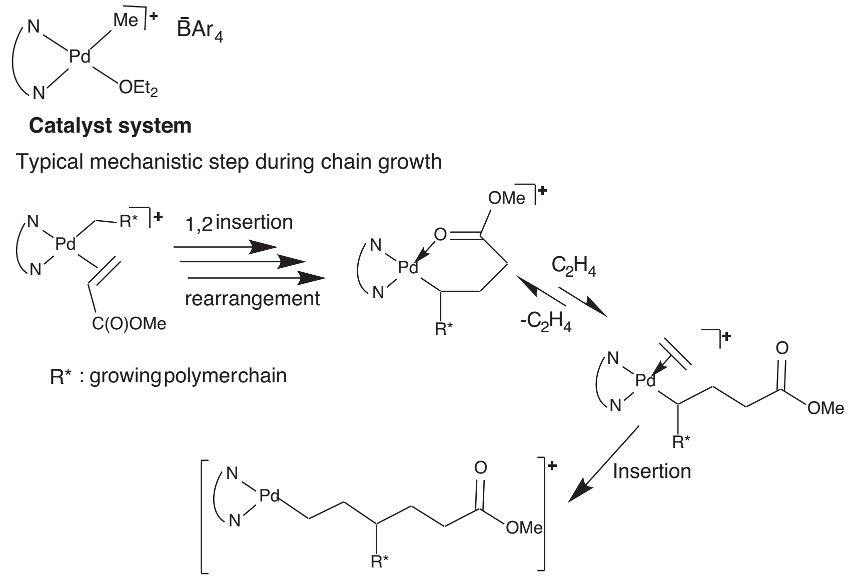
5.1 Palladium- and Nickel-Based Catalyst Systems

With the evolution of cationic Pd(II) and Ni(II) α-diimine catalysts, the olefin polymerization received a further boost. DuPont also commercialized this catalyst with trade name Versipol. These catalyst systems polymerized olefin and α-olefin and also copolymerized olefin with a range of functional olefins. The important features of these catalyst systems were the highly electrophilic and cationic Ni or Pd metal centers, use of bulky α-diimine ligands, and non-coordinating counterions. The electrophilicity of the metal centers improved the rate of olefin insertion, whereas the bulkiness of the ligands facilitated insertion in comparison with chain transfer. The non-coordinating counterions provided site for the olefin coordination. Easy and high-yield synthetic routes to α-diimine ligands allowed development a range of catalyst based on Ni(II) and Pd(II). The cationic form of the catalyst is essential for the catalytic activity. The catalyst precursor possessing a halide group was treated with salts of non-coordinating anions to synthesize the cationic species. For example, the α-diimine-Pd-chloride was reacted with NaBAF and stabilized with acetonitrile to synthesize a cationic catalyst (Scheme 8). However, attempts to use ether in place of acetonitrile resulted in the chloride-bridged dimers {[(N-N) PdMe]2-μ-Cl}BAF. Alternative routes were utilized to synthesize the cationic Pd and Ni ether complexes by opting for Pd or Ni dimethyl precursors (Scheme 8).

Subsequently, phosphine-sulfonate-based catalyst systems possessing broad functional group tolerance were developed by Brookhart to insert vinyl ethers [29], acrylonitrile [30], vinyl chloride [31], and vinyl acetate [32] in polyethylene chain. These active Ni(II)- and Pd(II)-based ligands of general formula $[(ArN{=}C(R)C(R){=}NAr)M(CH_3)(OEt_2)]^+BAr'_4{}^-]$ copolymerized ethylene and functional ethylene [33]. The polymerization initiation step via formation of the active species was much slower compared to that of the chain propagation favoring the polymerization. The aryl groups of the diimine ligand possessed bulky substituents that blocked associative olefin exchange and effectively minimized chain transfer. As per the proposed mechanism, a six-membered chelate formed after insertion of functional monomer via chelation of the carbonyl group that opened up on subsequent insertion of ethylene monomer, and the copolymerization occurred via repetition of the



Scheme 8 Synthesis of cationic catalysts for polymerization of functional olefins



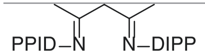
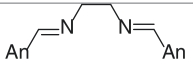
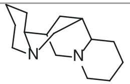
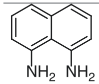
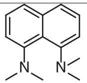
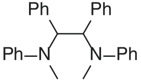
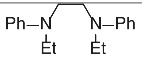
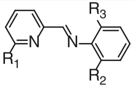
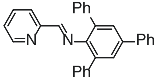
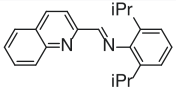
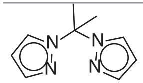
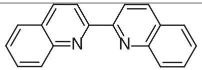
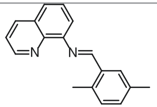
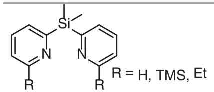
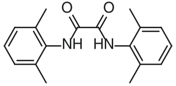
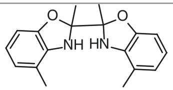
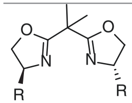
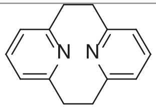
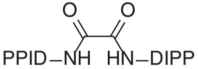
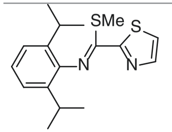
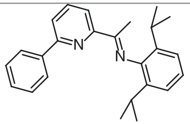
Scheme 9 The catalyst system used for copolymerization and a mechanistic step showing the insertion of monomers in the polymer chain

above steps (Scheme 9). However, the resulting copolymers were highly branched in nature due to extensive chain walking during polymerization.

Analogous Ni(II)-based catalyst and phosphine-sulfonate-based Pd(II) neutral catalyst systems produced linear copolymers. However, the neutral Pd(II) phosphine-sulfonate complexes were less reactive compared to the Pd(II) diimine-based catalyst system. The polymerization rate in case of the neutral Pd(II)-based system was improved by raising the polymerization temperature, and the higher temperature stability of the catalyst allowed higher polymerization. Subsequently, single-component catalyst systems based on P-O-chelated (PΛO) Pd(II) systems ligated with pyridine, lutidine, PPh_3, $Me_2NCH_2CH_2NMe_2$, and dimethyl sulfoxide were utilized to polymerize functional olefin monomers. The above studies revealed that the dimethyl sulfoxide (DMSO) binds less strongly to the metal center and gets readily displaced by olefin monomer facilitating the insertion process. This catalyst system allowed up to 50 mol% of acrylate insertion.

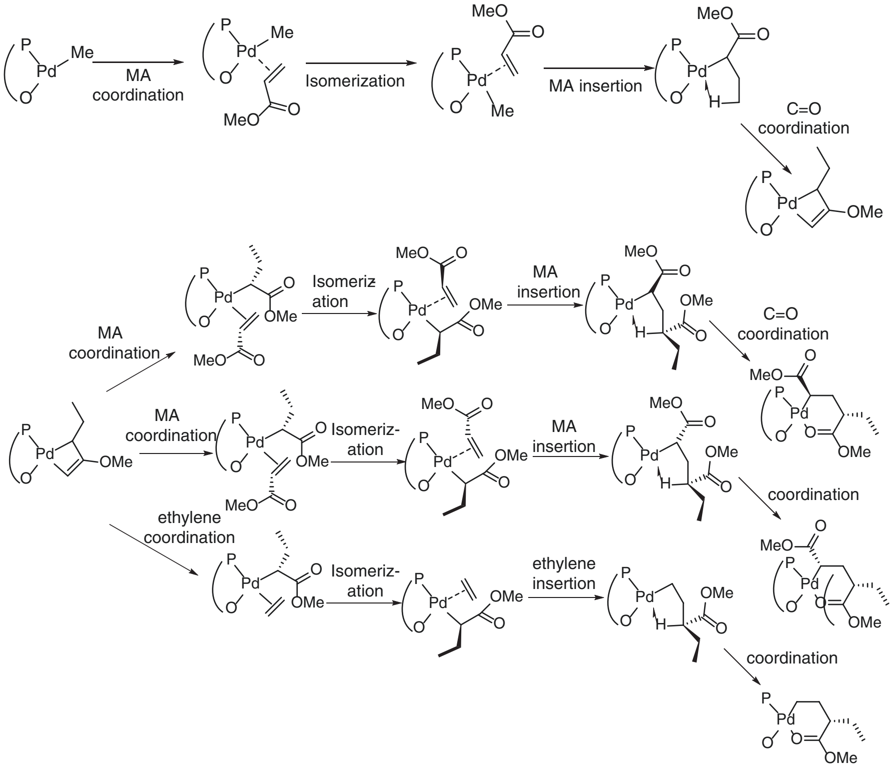
Further modification in catalyst structure allowed insertion of 1,1-bisfunctional vinyl monomers in the polyethylene chain. For example, Chikkali and coworkers synthesized an acetonitrile-ligated Pd-phosphine sulfonate complex that successfully incorporated up to ~9.6 mol% of ethyl-2-cyanoacryalate monomer in the polyethylene chain possessing a molecular weight value of ~3100 g/mol and a narrow polydispersity index value of 1.3 [34]. Subsequently, a range of NΛN-type ligands were developed and utilized to synthesize catalysts for this purpose (Table 6). Comparatively, the Pd-based catalyst systems produced high molecular weight polyolefin compared to that of the Ni-based catalyst system. The ethylene produced

Table 6 List of NΛN-type ligands utilized for development of Pd- and Ni-based catalyst systems

from the Pd-based catalyst systems is amorphous and highly branched in nature with density value up to 0.85. This allowed the researchers to produce blended polyethylene by using mixed catalyst systems. For example, combining a palladium α-diimine-based catalyst with a metallocene catalyst in a specific ratio, the crystallinity of resulting polyethylene may be controlled.

Mecking provided mechanistic insight into the acrylate insertion by studying the PΛO chelation-based system (Scheme 10) [35]. The relative binding strength of DMSO versus ethylene at 80 °C and 10 bar was determined to be 1.1×10^{-3}. He proposed that delayed displacement of the chelating carbonyl ligand via π-coordination of incoming monomer (equilibrium constant = 2×10^{-3} L/mol) substantially retards but allows polymerization. Importantly, the nature of ligand in the chelate has strong impact on the reaction entropy. The study further revealed that the second insertion of the acrylate or ethylene monomer is subjected to the dissociation of O-coordinated carbonyl moiety from the Pd center. The acrylate insertion was less favorable by 35 kJ/mol, whereas the insertion of ethylene moiety was favored by 41 kJ/mol. The overall study suggested the efficiency of the catalyst system towards copolymerization of the functional and non-functional olefin



Scheme 10 Initiation of the active site and possible pathways for the insertion of methyl acrylate (MA) or ethylene in the copolymerization process on (PΛO)Pd-based catalysts

monomer. Furthermore, the migratory insertion involves a cis-trans isomerization with the monomer remaining cis to P donor, which proceeded through a concerted step without dissociation. This also made the second acrylate insertion less favorable compared to that of the ethylene owing to steric factors.

These Pd- and Ni-based cationic catalyst systems were effective in polymerizing cyclo-olefins to produce crystalline polymers with molecular weight up to 251,000 g/mol. These polymers exhibited a broad melting temperature ranging from 241 to 330 °C. This is in contrast to the polymers derived using metallocene catalyst, which were not melt-processable. The chain growth in cyclopentene proceeded via insertion at the secondary alkyls. However, chain walking to methyl unit was noticed during polymerization of substituted cyclopentene. The diamine chemistry was extended to other metals such as Fe and Co, though these catalyst systems displayed low-to-moderate activity. Similarly, *N*,*N*′-ditrimethylsilylbenzamidinato, an amidinate ligand, is known to support Cu-catalyzed polymerization of ethylene [36]. A cupper chloride complex synthesized from hexamethyldisilazane, benzonitrile, and trimethylsilyl chloride and activated with methylaluminoxane-polymerized ethylene and the molecular weight was found to be 820,000 g/mol with melt temperature of 138 °C (Fig. 8) [37]. However, the 2,2′-bis[2-(1-ethyl benzimidazol-2-yl)biphenyl]copper-based system produced polyethylene of low molecular weight (M_n = 4900 g/mol) [36]. Subsequently, other polymerization techniques such as atom transfer radical polymerization were discovered for polymerization of active olefin monomers including acrylates and styrene.

5.2 *Catalysts Based on Tridentate Ligands*

The use of tridentate ligands was useful as the catalyst systems based on several tridentate ligands including pyridine bis(imine) (PBI), furan bis(imine), pyrrole bis(imine), and anionic amine and phosphine polymerized ethylene at fast rates to form linear high-density polyethylene (Fig. 9). Even at low ethylene pressures of 1 atm, the polymerization was highly exothermic, and the crystalline polyethylene swiftly precipitated from solution. As per the proposed mechanism, low barrier to insertion in these systems facilitated the polymerization process. A comparative analysis between Co- and Fe-based systems revealed that the activity of the cobalt PBI systems is independent of the ethylene pressure in the reactor (Table 7). Interestingly, the activity of the Fe-PBI-based system increased with the ethylene pressure [38]. Even the “R” group in the PBI affected the activity of the catalyst. These catalyst systems exhibited adequate thermal stability with reasonable lifetimes at 100 °C.

The bulkiness around the metal center in PBI-based Co and Fe complexes is a key parameter to retard the chain transfer process during polymerization and produce high molecular weight polymers. Reduction in ligand size by decreasing the size of ortho-substituents on the imine aryl group inhibits the polymer growth and causes a drop in the molecular weight of the resulting polymer. Overall, the Fe-based

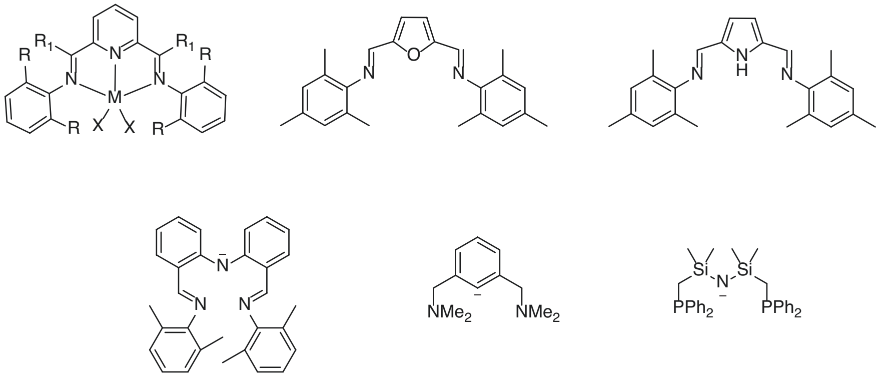


Fig. 9 Different tridentate and anionic tridentate ligands used for synthesis of Co- and Fe-based complexes

Table 7 Effect of ethylene pressure on the polymerization activity [39]

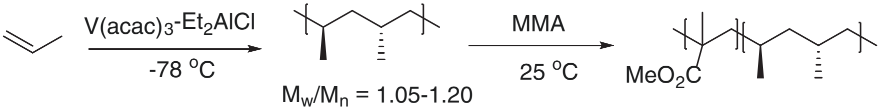
Metal	Ethylene pressure (atm)	Activity (kg of polyethylene/g of M/h)
Co	7	140
	41	140
Fe	7	1860
	41	4220
	340	11,900

complexes produce higher molecular weight polyethylene compared to that of the Co-based systems. Longer polymerization times and use of methylaluminoxane in low concentrations produced monomodal, narrow dispersity, and really high molecular weight polyethylene. The copolymerization of ethylene and propylene is sluggish in Fe-PBI-based systems. During homopolymerization of polypropylene, the regioregularity of polymer decreases with the decrease in steric bulk of ligands in the catalyst. These are the first reports on isotactic polypropylene synthesis via 2,1-insertion using late metal systems [40]. The PBI catalysts synthesized using small-size ligands, preferably possessing a single ortho-substituent on the imine aryl group, are known to produce high-quality polymers in absence of chain walking. The PBI oligomerization catalysts also exhibit high turnover frequencies (100,000 kg/g of Fe/h) [41]. Advantageously, these oligomerizations can be carried out over a large range of temperature and pressure and at a lower pressure compared to the previously utilized 11–200 atm. Use of similar tridentate ligands in Ru system exhibited low activity. For example, the complex based on pyridylbis (oxazoline) pyridine (pybox) and Ru produced 0.28–2.14 kg of polyethylene/mol of Ru/h at 25–60 °C and 6–12 atm [42]. This low activity was attributed to limited participation of Ru in the polymerization process.

6 Vanadium-Based Complexes for Precise Polyolefin Synthesis

It is well-known that in case of classical Ziegler-type catalyst system, the vanadium-based catalyst produced high molecular weight polyolefin with narrow molecular weight distribution at high activity (1000 kg PE/mol V h) [43]. The M_w/M_n value (1.5) of the polymer obtained from V-based catalyst was much lower compared to that of the Ti-based catalyst (15–30). This fact strongly suggested the formation of a single catalytically active species in this catalysis [44]. The V-based catalyst also allowed copolymerization of ethylene and propylene to produce high molecular weight amorphous polymers [45]. The catalyst system was subsequently extended to synthesis of ethylene/propylene/diene copolymers (EPDM), which were commercialized as synthetic rubbers [46]. The ethylene-cyclic olefin copolymers (COC) synthesized using V-based catalyst systems were commercialized as lenses for DVD recorders and camera phones by Mitsui Chemical, Inc. (APEL). The V(acetylacetonato)$_3$-Et$_2$AlCl catalyst system polymerized propylene to produce syndiotactic "living" polymer with low M_w/M_n value of 1.05–1.20 [47]. The breakthrough in functional polymer synthesis was achieved with the copolymerization of propylene with methyl methacrylate, although the catalytic activity was low (~4 kg of polymer/mol V h) (Scheme 11) [48].

Trivalent and tetravalent complexes based on V(III) are mainly utilized for the olefin polymerization processes. However, the V(III) is unstable and gets readily reduced to V(II) in presence of aluminum species. Therefore, the research mainly concentrated on stabilizing the V(III) form using suitable ligand system. For example, suitable modification of the β-diketonate (acac) ligand altered the catalytic activity of complexes during ethylene/propylene copolymerization (Table 8) [49].



Scheme 11 Syndio-specific propylene followed by diblock copolymer with methyl methacrylate synthesis using V(acac)$_3$-Et$_2$AlCl system

Table 8 Ethylene-propylene copolymer synthesis in presence of V(β-diketonate)$_3$-Et$_2$AlCl/Et$_3$Al$_2$Cl$_3$ catalyst system [50]

V cat.	V(acac)$_3$		V(Cy-acac)$_3$		V(*t*Bu-acac)$_3$		V(CF$_3$-acac)$_3$	
Al cocat.	Et$_2$AlCl	Et$_3$Al$_2$Cl$_3$	Et$_2$AlCl	Et$_3$Al$_2$Cl$_3$	Et$_2$AlCl	Et$_3$Al$_2$Cl$_3$	Et$_2$AlCl	Et$_3$Al$_2$Cl$_3$
Activity	1988	1960	2336	1980	1492	1244	1524	1600
$M_w \times 10^{-5}$	2.19	7.02	2.18	7.16	2.90	12.65	2.77	8.01
M_w/M_n	2.3	2.5	2.3	2.2	2.2	2.4	2.2	2.3
% ethylene	62	52	59	53	65	57	63	54

Reaction condition: vanadium 5 μmol, Al 0.2 mmol (Al/V = 40, molar ratio), Cl$_3$CCO$_2$ET 20 μmol, 200 mL of cyclohexane, ethylene/propylene = 2 bar, 22 °C, 30 min, activity (kg polymer/mol V h)

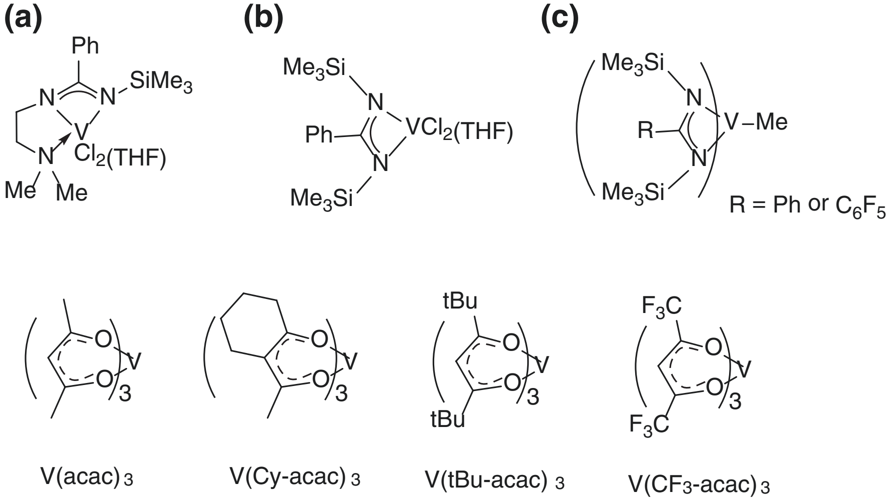
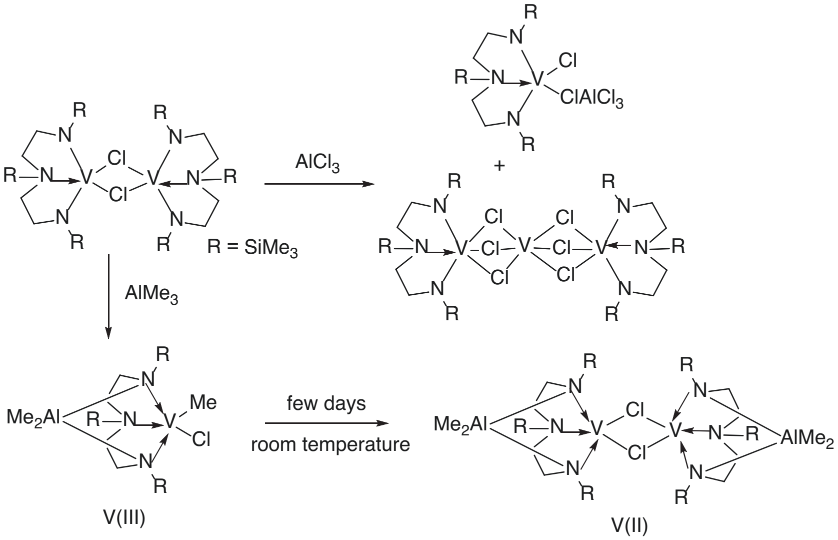


Fig. 10 (**a**–**c**) V(III)-based complexes utilized for olefin polymerization

However, use of β-diiminato ligands, such as [ArNC(R)CHC(R)NAr]-[R = Me, *t*Bu; Ar = Ph, 2,6-iPr$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$], displayed insignificant catalytic activities.

The catalyst systems based on V(III) possessing (dimethylamino)ethyl-functionalized benzamidinate ligand (Fig. 10a) along with Et$_2$AlCl displayed modest catalytic activity for polymerization of ethylene. The activity for above polymerization at 30 °C was 447 kg polymer/mol V h bar for ethylene loading of 6 bar. The activity (447 kg polymer/mol V h bar) of the complex based on {[PhC(NSiMe$_3$)$_2$]VCl$_2$(THF)}$_2$ (Fig. 10b) was somewhat lower under the same conditions [50]. On increasing the temperature, the activity of **10b** increased, whereas **10a** exhibited a decrease in catalytic activity. The V(III) complex based on **10b** and **10a** when placed on MgCl$_2$/AlEt$_n$(OEt)$_{3-n}$ support exhibited exceptional catalytic activity of 1490 kg polymer/mol V h bar and 3120 kg polymer/mol V h bar, respectively. V(III) methyl bis(amidinate) complex oligomerized ethylene (M_n = 1780, M_w/M_n = 2.3) without any additional co-catalyst. Replacing the Ph group with C$_6$F$_5$ further improved the catalytic activity (8.1 kg oligomer/(mol V h)) [51].

Subsequently, dinuclear catalyst systems were developed and analyzed. A dinuclear vanadium(III) chloride complex possessing a bis(amido)amine [(Me$_3$Si)NCH$_2$CH$_2$]$_2$N(SiMe$_3$) in presence of Me$_2$AlCl (activity = 660 kg polymer/(mol V h) or methylaluminoxane (activity = 237 kg polymer/(mol V h) exhibited strong catalytic activity for ethylene polymerization at 50 °C [52]. However, the lifetime of the catalyst was limited to 20–30 min only; this may be attributed to the conversion of V(III) to inactive V(II) species (Scheme 12). Similarly, other complexes based on V(III) species were synthesized and utilized for polymerization of ethylene (Fig. 11). For example, dithiolate ligand (**11a**, **11b**, and **11c**)-based complexes displayed catalytic activity up to 1990 kg PE/mol V h in presence of Et$_2$AlCl and MgCl$_2$ as



Scheme 12 The dinuclear V(III)-based complex and conversion to the V(II) species

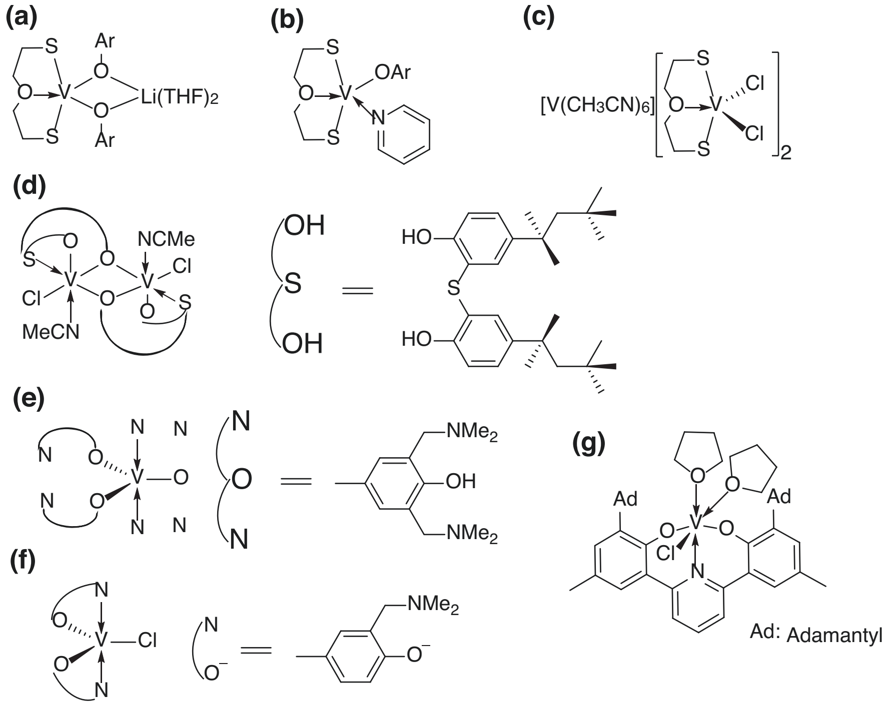


Fig. 11 (**a**–**g**) Chelated V(III) complexes utilized for polymerization of olefin

co-catalyst at ethylene pressure of 6 atm at 50 °C. The mixed-valence complex system (**11c**) exhibited lower activity (254 kg PE/mol V h) compared to that of the **11a** and **11b**. Replacement of dithiolato ligand with thiobis(phenoxy) moiety (**11d**) vastly improved the catalytic activity. The catalyst in presence of $\mathrm{Al}t\mathrm{Bu}_3$ as the co-catalyst exhibited a catalytic activity of 11,708 kg PE/(mol V h) for polymerization of ethylene [53].

V(III) complexes possessing O,N-chelating aminophenolate ligands (**11e** and **11f**) were tested as catalysts for ethylene polymerization. These systems in presence of Et_2AlCl and $EtAlCl_2$ co-catalysts exhibited moderate activity (27–159 kg PE/mol V h), and the molecular weight of the resulting polymer was relatively high ($M_w = 6.7 \times 10^5$) [54]. Bis(phenoxy)pyridine ligand-based V(III) complex (**11g**) along with methylaluminoxane co-catalyst was suitable for polymerization of propylene with activity value of 803 kg polymer/(mol V h) [55]. The polypropylene produced under 5 atm propylene pressure and 0 °C exhibited M_w value of 1.17×10^6 with $M_w/M_n = 2.03$. Complexes based on V(IV) and V(V) states were later synthesized and utilized as the catalyst for ethylene polymerization along with co-catalysts. The (arylimido)-V(IV)Cl_2 complexes in combination with Et_2AlCl exhibited adequate activity for polymerization of ethylene, and the resulting polymers displayed uniform distribution of molecular weight (Fig. 12a) [56].

A bis(amide)-based V(IV) complex was effective for copolymerization of ethylene and propylene (Fig. 12b). The nature and amount of aluminum-based co-catalyst controlled the activity of the system [57]. Use of Et_2AlCl and $EtAlCl_2$ exhibited maximum activity (860 kg polymer/mol V h) compared to that of the individual ones (80–330 kg polymer/mol V h). Complexes were also synthesized using salen-type tetradentate ligands (Fig. 12c). However, the polyolefins obtained using the catalyst system displayed broad molecular weight distribution in the range of 7.3–10.4 [58]. The V(V) complexes were synthesized using $VOCl_3$ as the precursor.

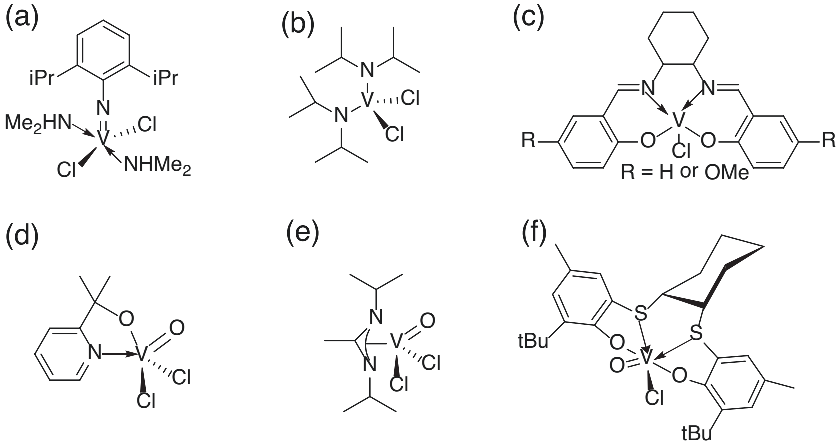


Fig. 12 (**a–f**) Catalyst systems based on vanadium(IV) and vanadium(V) species for olefin polymerization

Among several complexes studied, the complex based on O,N chelate exhibited high activity (642 kg polymer/mol V h) towards ethylene polymerization in presence of Et_2AlCl (Fig. 12d) [59]. However, conversion of the V=O group in the complex to V=N-Ph-Me compromised the activity of the system. Amidinate-based V(V) Cl_2 complexes were studied for copolymerization of propylene and 1,3-butadiene (Fig. 12e). The polymerization was effective at −60 °C and produced syndiotactic-rich polymer in presence of Et_2AlCl co-catalyst and atactic polymer in presence of methylaluminoxane co-catalyst [60]. An oxovanadium complex based on O,S,S,O chelation exhibited high activity for ethylene polymerization (Fig. 12f) [61]. Similar studies supported that aromatic-O- and aromatic-N-based ligands stabilized the vanadium-based complexes in presence of Al-based co-catalyst. $VO(OR_3)$ complexes based on tetradentate ligands possessing phenolic moieties exhibited extremely high activity (96,500 kg polymer/(mol h bar) towards ethylene polymerization to produce polyethylene with very high molecular weight ($M_w = 5.18–8.67 \times 10^6$ g/mol) (Fig. 13a). A dimeric complex of $[VO(OR_3)]_2$ type also displayed high activity (123,000 kg of polymer/mol h bar) for ethylene polymerization in presence of Me_2AlCl and Cl_3CCO_2Et at 80 °C (Fig. 13b). Oxo complexes based on calyx-[3]arenes were synthesized from the vanadium alkoxide precursors (Fig. 13c).

The resulting catalysts produced polyethylenes of very high molecular weight under ambient temperature conditions [62]. Vanadium(V) complexes possessing a combination of arylimido and aryloxo ligands were synthesized and utilized for polymerization of ethylene in presence of methylaluminoxane as the co-catalyst by

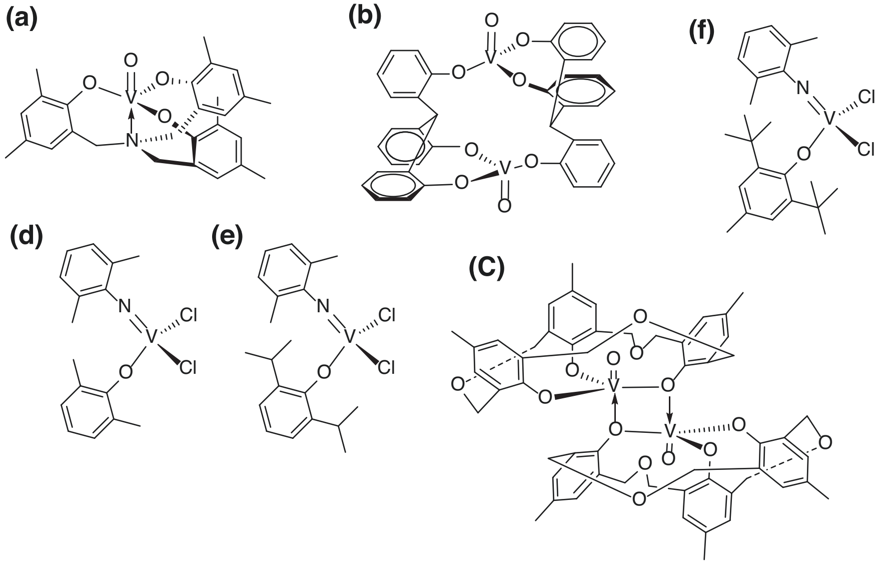


Fig. 13 (**a**–**f**) The range of catalysts based on vanadium(V) for polymerization of ethylene and copolymerization of olefins

Table 9 Ethylene polymerization data using 13d–f as the catalyst and methylaluminoxane as the co-catalyst in toluene solvent [64]

Complex	Temperature (°C)	Activity (kg/mol V h)	$M_w \times 10^{-5}$ (g/mol)	M_w/M_n
13d	25	1770	2.73	4.65
13d	25	2930	17.5	1.64
13e	25	1050	2.38	4.92
13e	0	576	60.9	2.61
13e	25	967	20.3	2.73
13e	40	348	–	–
13f	25	242	–	–
13f	60	486	7.84	2.07

Nomura and coworkers (Fig. 13d–f) [63, 64] The complex systems produced polyethylenes with molecular weight in the range of 2.38–60.9 × 10^5 g/mol and relatively narrow polydispersity index values in between 1.64 and 4.65 (Table 9). The activities of the above complexes were observed in the range of 242–2930 kg of polymer/mol h bar.

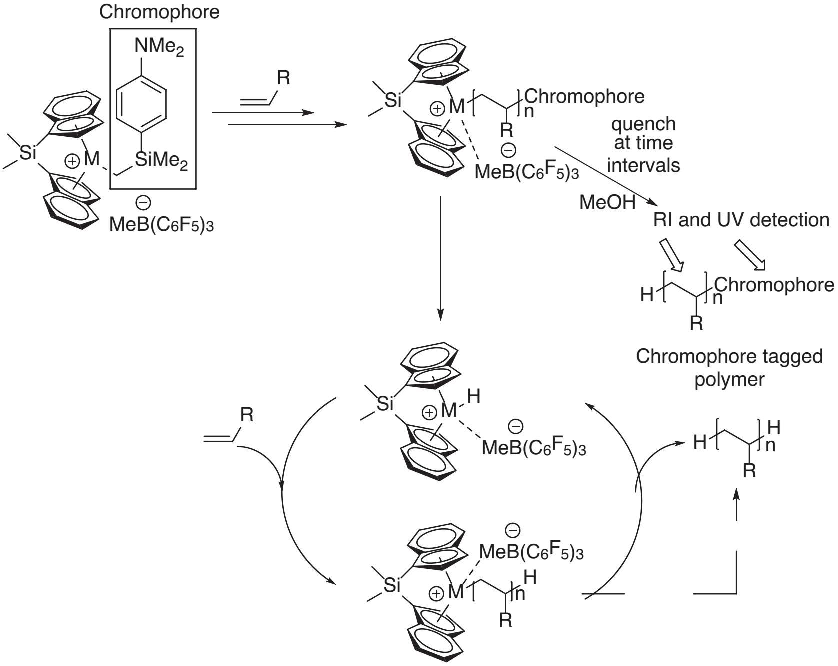
7 Recent Advances

The Ziegler-Natta catalyst has undergone extensive transformation since inception, and a range of ligand and metal combinations along with co-catalysts have been investigated in detail. The catalyst systems have been developed to precisely control the stereoselectivity of the resulting polymer. The advancement in catalyst structure has rendered the synthesis of poly-α-olefins with precise tacticity. The $MgCl_2$-supported Ti-based catalyst composition has reached up to the sixth generation via modification of internal and external donor species (Table 10). Catalysts are available to synthesize random and block copolymers of olefins and selectively polymerize a particular olefin in a mixture of olefin monomers. Especially, the role of metallocenes in the catalysis and chelated complex systems can be considered as landmark innovations in the area. The research area is still attracting a substantial attention of researchers, and a large number of publications are emanating from the research conducted in the area. Involvement of advanced spectroscopic and microscopic characterization tools has made this possible to characterize the catalyst systems and resulting polymers. This has facilitated to draw the structure-property relationship of the synthesized catalyst systems. The origin of stereoselectivity is unraveled by using a set of sterically related external donors and correlating the amount of a particular stereo block in the resulting polymers via high-throughput screening. The internal structure of the catalyst system is determined with the help of machine learning by using a genetic algorithm and density functional calculations [65]. High-throughput experimentation is also utilized to understand the hydrogen response of propylene polymerization [66].

The number of active sites in the catalyst plays a crucial role in controlling the molecular weight distribution and tacticity of the polymers. Recently, methyl

Table 10 $MgCl_2$-supported Ti-based Ziegler-Natta catalyst system and resulting polymer properties [66]

Generation	Internal donor	External donor	Productivity × 10^{-3} (kg of polymer/g of Ti)	M_w/M_n
Third	Ethyl benzoate	Aromatic monoester	0.5–0.8	6–9
Fourth	Diethyl phthalate	Alkoxysilane	1–2	6–8
Fifth	2,2′-Dialkyl-1,3-dimethoxypropane	None or alkoxysilane	>2	4–6
Sixth	Dialkyl succinate	Alkoxysilane	1–2	>8



Scheme 13 Chromophore labeling technique to estimate the molecular weight of growing polymer chain at regular intervals

propargyl ether possessing ~100% labeling efficiency was used as a labeling agent via a coordination-insertion reaction to count the number of active sites in the catalyst [67]. Lately, single-site group four metal-based catalysts are developed to control the polymerization and stereochemistry of the product. Kinetic modeling is currently carried out to understand the polymerization pathway and possible intermediates formed during the course of reaction [68]. Chromophore labeling technique is utilized to understand the polymer growth rate using size exclusion chromatography (SEC). Presence of chromophore at the chain end enabled the polymer chain to be detected using UV detector in the SEC analysis (Scheme 13) [69]. Other techniques such as quench labeling with radioactive element such as tritium, MeOD, ^{14}CO, etc. are utilized to understand the growth rate of the polymer chain.

Advanced techniques such as 3D X-ray ptychography and X-ray fluorescence tomography are recently utilized to understand the fragmentation behavior of catalyst and radial distribution of metal in the catalyst-polymer particles and continuous bisection of the catalyst particles during polymerization [70]. A combination of two homogeneous catalysts is utilized as an approach to synthesize disentangled ultra-high molecular weight polyethylene. The synergy between Ti^{3+} and Al^{3+} is established using a set of physicochemical and spectroscopic techniques to further understand the chain growth during polymerization [71]. Overall, the field of Ziegler-Natta catalysis is unraveling exciting avenues to contribute towards the quality of polyolefins produced in terms of thermos-mechanical properties and exhibit sufficient promise of being extended to synthesis of other polymeric systems in future.

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