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Evolution of Ultra High Molecular Weight Polyethylene Synthesis: A Comprehensive Review of Phenoxy-Imine Catalysts for Enhanced Material Properties and Industrial Perspective

Gediz Korkmaz[1,#]

More than 60 years after its first synthesis, Ultra High Molecular Weight Polyethylene (UHMWPE) remains a material of choice for numerous applications in biomedical, energy storage, and industrial parts manufacturing. Its basic and inert chain structure, semi-crystalline morphology, low friction coefficient, and wear-resistant properties make it an ideal candidate for knee and hip joints, battery separators, and low-wear, low-friction equipment parts. The properties of UHMWPE change significantly with variations in molecular weight, polydispersity, and chain entanglements. Therefore, the choice of catalyst-cocatalyst-scavenger systems in UHMWPE production plays a crucial role in determining the material's properties and quality. Since the late 1990s, the development of the 'ligand-based catalyst development strategy' and the introduction of the Phenoxy-Imine (FI) ligated Titanium catalyst by Fujita and coworkers have prompted many researchers to focus on FI catalysts and their applications in UHMWPE synthesis. Disentangled Ultra High Molecular Weight Polyethylene (dUHMWPE) synthesized using specific FI catalysts, particularly those with fluoroaniline-containing ligands, have exhibited very high activity and demonstrated 'living polymerization' characteristics. This study provides a concise review of UHMWPE catalysts, with a special emphasis on the phenoxy-imine class of post-metallocene catalysts.

1. Introduction

Ultra High Molecular Weight Polyethylene (UHMWPE) is a specialty thermoplastic polymer that shares a similar chemical structure with High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE), both of which are commercial polymers. However, UHMWPE differs significantly in its physical properties. Due to its low coefficient of friction, inertness, and chemical stability, UHMWPE is considered the material of choice for total joint replacement operations [1]. Additionally, its exceptionally high tensile properties make UHMWPE a widely used fiber material in the biomedical, industrial, and marine industries. Furthermore, its chemical stability and semi-crystalline structure make UHMWPE an excellent candidate for Li-ion battery separators [1].

UHMWPE was first synthesized in 1955 and commercialized the same year by Ruhrchemie AG in Germany. At that time, UHMWPE was synthesized using a first-generation Ziegler catalyst, unsupported $TiCl_3$. Later, towards the end of the 1960s, the development of the $MgCl_2$-supported $TiCl_4$ catalyst revolutionized the polyethylene industry, leading to the widespread adoption of this high-activity, supported catalyst type, including for UHMWPE synthesis. However, the use of UHMWPE was initially limited due to its high molecular weight, increased number of entanglements, and relatively low degradation temperature. Processing UHMWPE was challenging and restricted to a few methods, primarily variants of ram extrusion. The introduction of gel spinning technology to UHMWPE enabled the production of very strong and lightweight fibers, significantly expanding its market applications [2]. Today, fibers and

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[1]Cukurova University, Graduate School of Sciences, Department of Advanced Materials and Nanotechnology, 01330 Adana, Türkiye

#Corresponding author: gkorkmaz@student.cu.edu.tr

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composites of UHMWPE represent the second largest segment of the UHMWPE market [3].

In 1980, Kaminsky and Sinn first utilized Methylaluminoxane (MAO) as a co-catalyst/scavenger with a single-site, homogeneous metallocene catalyst, specifically a titanocene compound. This invention marked a new era in polyolefin synthesis, including UHMWPE synthesis. This catalyst/co-catalyst pair also illuminated pathways for future research in polyolefin synthesis [4-6]. Following the breakthrough with metallocene catalysts, scientists began exploring new ligand configurations around the metal center, leading to the development of constrained geometry catalysts (CGCs). Dow Chemical Company successfully deployed CGCs in the production of polyethylene and polyolefin elastomers, branding this innovation as INSITE Technology [7, 8].

Finally, towards the end of the 1990s, Fujita and co-workers introduced phenoxy-imine (FI) catalysts. These catalysts were based on an octahedral molecular structure and utilized Ti, Zr, or Hf (Group IV transition metals) as the metal center [9, 10]. Concurrently, many researchers focused on alternative polyolefin catalysts using non-Group IV transition metals. Notably, Ni and Pd-centered late transition metal catalysts proved successful in polymerizing olefins. A distinguishing feature of these late transition metal catalysts was their ability to incorporate polar monomers into the polyolefin backbone without exhibiting poisoning behavior [11].

2. UHMWPE Synthesis with Ziegler Natta Catalyst

$MgCl_2$-supported Ziegler-Natta catalysts remain the workhorse of the polyolefin market, including UHMWPE. Their availability and lower cost make them a viable option for commercial polyolefin grades as well as for many UHMWPE grades. In response to the demand for $MgCl_2$-supported Ziegler-Natta catalysts, $MgCl_2$ support technology has also advanced. For example, a well-known and reputable Japanese UHMWPE producer continues to use Ziegler-Natta catalyst technology to produce submicron-sized $MgCl_2$ catalyst supports and micron-sized UHMWPE particles. They achieve this by utilizing controlled precipitation of the support using $MgCl_2$ adducts [12]. In the academic context, many researchers have studied UHMWPE synthesis using Ziegler-Natta catalysts.

In 2001, Velikova used SiO_2 as the support for $TiCl_4$ and $VOCl_3$ to synthesize UHMWPE [13]. SiO_2 is a well-known support material for Cr-based HDPE catalysts and for many metallocene and constrained-geometry catalysts [13, 14]. Velikova synthesized five catalysts containing titanium and vanadium metal centers and activated them with diethylaluminum chloride (DEAC) and butyl-octyl magnesium (BOM). Velikova achieved higher yield and efficiency with the titanium catalyst, while the molecular weights of UHMWPE samples with vanadium catalysts were higher. Overall catalyst performances are given in Table 1. As expected, the supported catalysts were more effective than homogeneous catalysts. Subsequently, Velikova performed IR spectroscopy on the UHMWPE samples to determine the percentage of carbonyl groups present, as well as DTG and DTA analyses to define the thermal properties of the UHMWPE samples [13]. In 2008, Jamjah et al. synthesized UHMWPE using a MgCl2-supported $TiCl_4$ catalyst with tri-isobutylaluminum (TIBAL) as a co-catalyst [15]. TIBAL was selected to reduce chain transfer. They investigated the effects of temperature, monomer pressure, [Al]/[Ti] molar ratio, and polymerization time on the molecular weight and productivity of the catalyst.

Jamjah et al. concluded that using the proposed Ziegler-Natta catalyst-co-catalyst system and slurry polymerization technique, with careful selection of the Ti:Al ratio (catalyst/co-catalyst ratio) and process parameters, UHMWPE products with molecular weights ranging from 3×10^6 to 9.3×10^6 g/mol can be obtained; the effects of these process parameters are given in Figure 1 (a-e) [15].

In 2009 and 2010, Padmanabhan and co-workers published three consecutive studies on UHMWPE synthesis using a $MgCl_2$-supported Ziegler-Natta catalyst [16-18]. In the first study, they synthesized five different catalysts with varying Ti content [17].

Table 1. Vanadium and Titanium-centered homogeneous and supported catalysts and co-catalysts and their performances [13].

Catalyst	Catalyst System	Supp.	Ti or V Concentration (mmol/dm3)	Ti or V/Al/Mg Ratio	PE Yield (g)	Catalyst Efficiency (kg PE/g Ti or V)	Molecular weight ($x10^6$)
Ti-Cat 1	$TiCl_4$:DEAC:BOM	no	0.05	1/20/5	119.7	50	1.8
Ti-Cat 2	$TiCl_4/SiO_2$:DEAC:BOM	yes	0.021	1/60/30	96.9	96.3	1.2
Ti-Cat 3	$TiCl_4/SiO_2$:DEAC:BOM	yes	0.021	1/100/60	122.7	122	2.1
V-Cat 1	$VOC1_3/SiO_2$:DEAC:BOM	yes	0.039	1/20/8	69.5	35	5.3
V-Cat 2	$VOC1_3$:DEAC:BOM	no	0.07	1/10/6	30.6	8.6	2

Initially, they synthesized a Ti:$MgCl_2$ catalyst with a 20:80 ratio, which was used as the basis and activated with AlRR'$_2$, where R and R' are isoprenyl and isobutyl in equal amounts. By activating with different quantities of AlRR'2, they obtained four active catalysts (C-2 to C-5) with Ti3+ contents of 16%, 21%, 25%, and 32%. They synthesized UHMWPE by varying the ethylene pressure (PC2), catalyst employed (C-2 to C-5), and hydrogen pressure (PH2) in the reactor, using hexane as the reaction medium [17].

Padmanabhan and co-workers concluded that under PC2 reactor conditions, catalysts C-2 and C-3 are optimal for achieving better particle size distribution (PSD), as shown in Fig.2(a). With increasing ethylene pressure, the productivity of the catalysts also increases, as illustrated in Figure 2b. At 7.5 atm ethylene pressure, all catalysts produced UHMWPE with molecular weights in the range of 6 ×10^6 to 7 ×10^6 g/mol, as shown in Fig.2(c) [17].

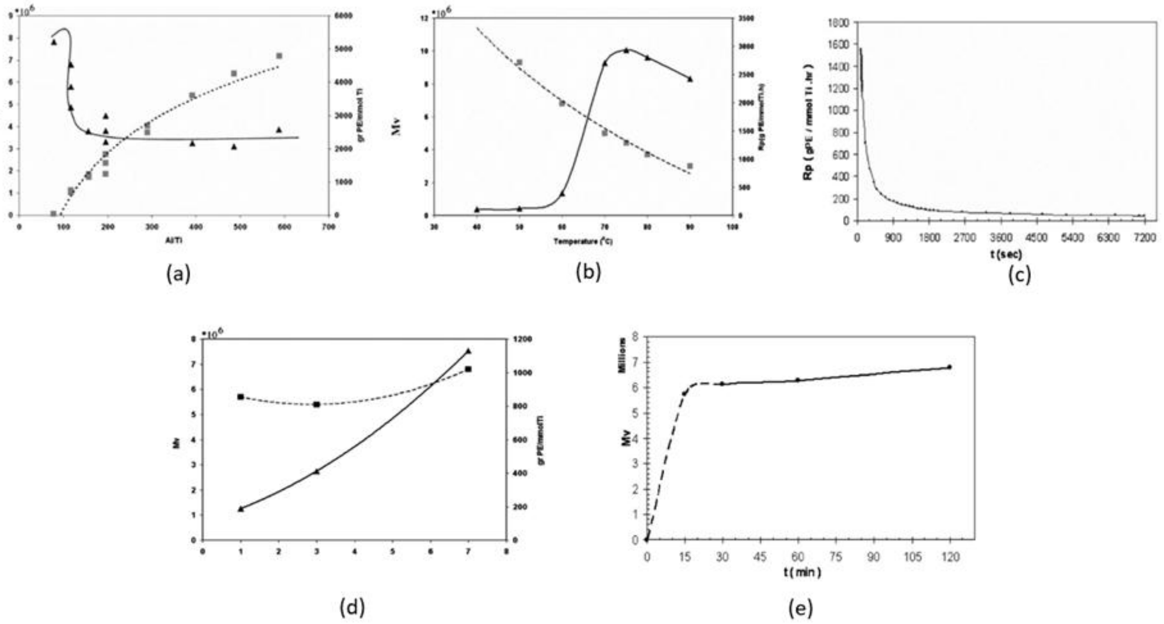


Figure 1. (a) Effect of [Al]:[Ti] on productivity of the catalyst and Mv of the polymer obtained.(b) Effect of temperature reaction on productivity and the Mv of the polyethylene polymerization. (c) Rate/time profile of the reaction. Polymerization conditions; temperature at 40^{0}C, monomer pressure at 4 bars, polymerization time 2h, [Al]:[Ti] ratio 117:1. (d) Effect of monomer pressure on both activity and Mv of the obtained polymer. (e) Effect of polymerization time on the Mv. Polymerization conditions; temperature at 60^{0}C, monomer pressure at 7 bars. (Reprinted from Macromol. Symp. 2008, 274, 148–153 with permission of John Wiley and Sons) [15].

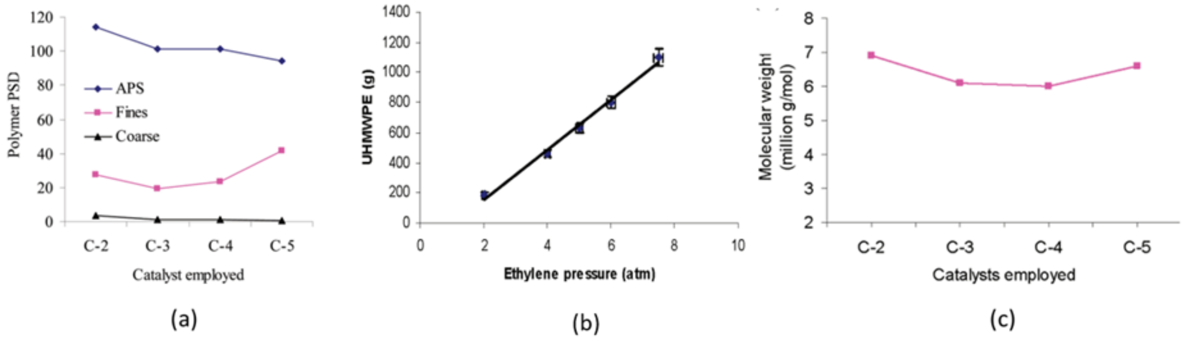


Figure 2. (a) Particle size distribution of UHMWPEs obtained with C-2, C-3, C-4 and C-5 catalysts.(b) Productivity of a typical catalyst at 5 different ethylene pressure (2 atm to 7,5 atm) conditions. (c) Molecular weights of UHMWPEs obtained with C-2, C-3, C-4 and C-5 catalysts at 7.5 atm C2 pressure (Reprinted from Macromol. React. Eng. 2009, 3, 257–262 with permission of John Wiley and Sons) [17].

They also explored the effect of H_2 on molecular weight at 5 atm and 7.5 atm ethylene (C2) pressure [17]. As expected, the results at 7.5 atm C2 pressure were better than those at 5 atm. Finally, they investigated the scale-up effect by conducting experiments in 1L, 5L, and 19L reactors. They observed that the 1L reactor, with fewer aluminum alkyls, produced a higher molecular weight polymer. They concluded that effective control of the alkyl aluminum concentration is an important parameter for UHMWPE synthesis [17].

In their second study in 2009, Padmanabhan and colleagues investigated various process conditions using similar catalyst systems to their previous work; specifically, they employed a $TiCl_4/MgCl_2$ system with Ti^{3+} contents ranging from 16% to 50%, along with a co-catalyst mixture of 50% triisobutylaluminum and 50% isoprenyl aluminum [18]. Initially, they synthesized a catalyst with 0% Ti^{3+} and adjusted the Ti^{3+} content using the co-catalyst mixture. Additionally, they explored the use of a commercial polypropylene (PP) catalyst as the primary catalyst and triethylaluminum (TEAL), widely used in the polyolefin industry, as the co-catalyst. The PP catalyst, employed at 7.5 atm ethylene (C2) pressure, produced very high molecular weight polyethylene with high yield, although the particle sizes were more than two-fold larger than UHMWPE synthesized with the C-21 catalyst (21% Ti^{3+}). Due to the higher chain transfer with TEAL, the polymers produced with the C-21 catalyst and TEAL were closer in properties to high-density polyethylene (HDPE) than UHMWPE [18].

Once again, Padmanabhan and colleagues investigated the same catalyst system, comprising 25% Ti^{3+} and a co-catalyst mixture of 50% triisobutylaluminum and 50% isoprenyl aluminum, for the synthesis of UHMWPE, but this time using a different solvent, varsol [16]. The primary objective of this study was to examine the solubility of ethylene and hydrogen in varsol and their impact on the polymerization reaction. In hexane, the solubility of ethylene decreases sharply with increasing hydrogen concentration, whereas in varsol, the presence of hydrogen in the solvent also enhances the solubility of ethylene [16].

In 2010, Yoon, Lee, and their colleagues, Shin et al, investigated the effect of polymerization temperature and pressure on the properties of UHMWPE [19]. They employed two different main catalysts: the first was $MgCl_2$-supported $TiCl_4$ with no internal donors and a Ti content of 6% (referred to as CatA), and the second was $MgCl_2$-supported $TiCl_4$ with di-sec-butyl-succinate internal donor and a Ti content of 2.7% (referred to as CatB). Triethyl aluminum was utilized as the cocatalyst, with all catalysts and cocatalysts supplied by a Korean chemical company. Polymerization runs were conducted at 20°C, 40°C, and 60°C. The highest activity observed among all trials was with CatA at 40°C, with catalytic activity decreasing beyond this temperature. Molecular weight was highest at 20°C and decreased with increasing reaction temperature. As expected, an increase in ethylene pressure led to an increase in the molecular weight of the UHMWPE samples [19].

In another study conducted in 2011, Yoon, Lee, and their colleagues, Zhang et al, investigated the effects of internal and external donors on the molecular weight and polydispersity index of UHMWPE [20]. They synthesized four different Ziegler-Natta catalysts: CatA (6% Ti with no internal donor), CatB (1.8% Ti with di-n-butyl phthalate internal donor), CatC (2.7% Ti with di-sec-butyl succinate internal donor), and CatD (3.8% Ti with 1,3-diether internal donor). Triethyl aluminum (TEAL) was utilized as the cocatalyst to initiate the polymerization. The study revealed that internal donors had an observable effect on catalytic activity, whereas external donors had no discernible effect on activity. The catalyst without an internal donor (CatA) exhibited the highest activity, followed by the catalyst with a succinate-type internal donor (CatC) with the second-highest activity. The catalyst with a phthalate donor (CatB) showed the third-highest activity, while the catalyst with a diether-type donor (CatD) exhibited the lowest activity. In terms of molecular weights, CatC produced UHMWPE with the highest molecular weight, followed by CatB, CatD, and finally CatA, which yielded the lowest molecular weight [20].

In a subsequent study conducted in 2012, Yoon, Lee, and their colleagues, Zhang et al, investigated the effect of co-catalysts on the structure of UHMWPE [21]. They employed the same catalysts (CatA - 6% Ti with no internal donor, CatB - 1.8% Ti with di-n-butyl phthalate internal donor, CatC - 2.7% Ti with di-sec-butyl succinate internal donor, CatD - 3.8% Ti with 1,3-diether internal donor) as the primary catalyst and utilized four different co-catalysts: triethyl aluminum (TEAL), triisobutyl aluminum (TIBAL), trioctyl aluminum (TOAL), and diethyl aluminum chloride (DEAC), along with their binary mixtures. Additionally, they examined the effect of hydrogen on the molecular weight and polydispersity index. Hydrogen is a commonly used chain transfer agent in the polyolefin industry, and as expected, the researchers observed that increasing hydrogen concentration resulted in a decrease in the molecular weight of the UHMWPE samples and an increase in their polydispersity. Yoon, Lee, and their colleagues noted that the alkyl chain length of the co-catalyst influenced the activity of the main catalyst, with increasing chain length leading to a decrease in catalyst activity. They ranked the alkyl aluminums in terms of their activities as TEAL > TIBAL > TOAL > DEAC. The difference in activity is attributed to the prevention of Ti and Al metals from coming closer, thereby reducing alkyl-chlorine exchange, as explained in the work of Gupta and Ravindranathan [21, 22]. However, when DEAC is mixed with TIBAL or especially with TOAL, catalyst activity increases considerably, indicating a synergistic effect [21].

Ruff and Paulik investigated the multistage polymerization of polyethylene to obtain reactor blends of ultra-high molecular weight polyethylene (UHMWPE) and medium-weight polyethylene (MWPE) at high pressure (20 bar) [23-25]. They employed a commercial Ziegler-Natta (ZN) catalyst typically used for isotactic polypropylene (iPP) production as the primary catalyst, although the type of internal donor used was not specified in the study. The ZN catalyst was activated by triethyl aluminum (TEAL). In their approach, UHMWPE was first produced in the initial reactor after a pre-polymerization step, followed by the introduction of hydrogen in the second reactor for chain transfer. The final product in this study was not UHMWPE. The results of their study were presented in three separate papers. The first paper described the polymerization process, polymerization kinetics, and properties of UHMWPE in the first reactor [23]. The second paper detailed the particle design and morphology of the reactor blends, with investigations conducted using scanning electron microscopy (SEM), particle size analysis, and bulk density measurements [24]. The final paper focused on the mechanical properties of the UHMWPE-MWPE blends. Ruff and Paulik compressed the reaction powder using compression molding and conducted characterization tests and dynamic mechanical analysis on the samples [25].

Severn and colleagues, Philippaerts et al, conducted a study in 2017 on the effect of support particle size on polymerization and the properties of ultra-high molecular weight polyethylene (UHMWPE) [26]. They synthesized $MgCl_2$ supports with five different particle sizes, ranging from 1.5 μm to 11.9 μm, by adjusting the stirring speed during support preparation. Particle properties such as bulk density, mean particle diameter, span, surface area, and pore volume were measured for the supports. Subsequently, $TiCl_4$ was impregnated onto the $MgCl_2$ supports, and polymerization tests were performed using triethyl aluminum (TEAL) as the co-catalyst. The characteristics of obtained supports are tabulated in Table 2 [26].

Severn and colleagues concluded that stirring speed does not have a significant effect on porosity and surface texture. However, they observed that support size had a notable effect on catalyst activity, with smaller support particles resulting in higher catalyst activity; the polymerization performances of the obtained catalyst particles are presented in Table 3 [26].

Additionally, in 2017, Severn and colleagues, Lafleur et al, extended their study to the area of constrained geometry catalysts. Using the same support structure and preparation method, they impregnated a single-site molecular catalyst onto $MgCl_2$, which will be outlined in the constrained geometry catalysts section of this review [27].

Wang and colleagues, Zhang et al, conducted a study to determine the effects of polymerization parameters on particle morphology, structure, swelling/dissolution, and rheological properties [28]. They utilized the standard $TiCl_4/MgCl_2$ and triethyl aluminum (TEAL) catalyst system to conduct polymerization studies of UHMWPE. Two methods were employed: i) pre-polymerization and ii) direct polymerization. Wang and colleagues concluded that pre-polymerized UHMWPEs are more densely packed and exhibit a correlation between particle size and molecular weight. In contrast, direct-polymerized UHMWPEs do not show this correlation [28].

Table 2. $MgCl_2$ support preparation results (Reprinted from Journal of Polymer Science, Part A: Polymer Chemistry 2017, 55, 2679–2690 with permission of John Wiley and Sons) [26].

No	Catalyst Type/Name	Stirring Speed $MgCl_2$ Batch (rpm)	Catalyst d50 (μm)^a	SPAN^a	S_{BET} (m^2/g)^b	V_{pore} (cm^3/g)^b	Mean Nodule Size (mm)^c
1	TMC-H-250	250	11.9	1.1	176	0.42	1.1 (5)(A)
2	TMC-H-500	500	6.5	0.9	152	0.36	0.9 (22)(A)
3	TMC-H-800	800	3.6	1.0	183	0.45	0.7 (21)(B)
4	TMC-H-1200	1200	2.4	1.4	175	0.43	0.7 (16)(B)
5	TMC-H-1400	1400	1.5	1.8	158	0.41	0.5 (6)(C)

^{a}Mean particle size and SPAN as obtained via DLS.

^{b}Obtained via N_2-physisorption.

^{c}Based on SEM: averages are taken from different measurements, the amount of nodules measured (N) is given in between brackets. Means that do not share a letter are significantly different.

Table 3. Polymerization performances of different catalysts with different support sizes (Reprinted from Journal of Polymer Science, Part A: Polymer Chemistry 2017, 55, 2679–2690 with permission of John Wiley and Sons) [26].

No	Catalyst	Catalyst Mass (mg)	Polym. Yield (g)	k_pC^* (1/(h M))	k_i (1/h)	k_d (1/h)	Polymer d50 (μm)
1	TMC-H-250	15	120	12485	0.9	0	161
2	TMC-H-500	15	228	20518	1.9	0	116
3	TMC-H-800	15	307	23582	1.8	0	93
4	TMC-H-1200	15	393	49944	1.3	0.3	62
5	TMC-H-1400	7	282	63055	1.7	0.2	60

All reactions were performed at 60^0C, under a constant pressure of 5 barg. All experiments were stopped after a total polymerization time of 2 h.

3. UHMWPE Synthesis with Homogeneous Catalysts

3.1. Metallocene based UHMWPE synthesis

In 2000, Alt and Köppl conducted a comprehensive review on group IV metallocene catalysts for ethylene and propylene polymerization [29]. They concluded that the bite angle and bulky substituents on the ligands affect the activity sterically by limiting free coordination space, which is necessary for β-hydride elimination. Additionally, the stability of the metal center-carbon bond plays a role; hafnium has more stable metal-carbon bonds than titanium and zirconium, thereby favoring the production of higher molecular weight polymers [29].

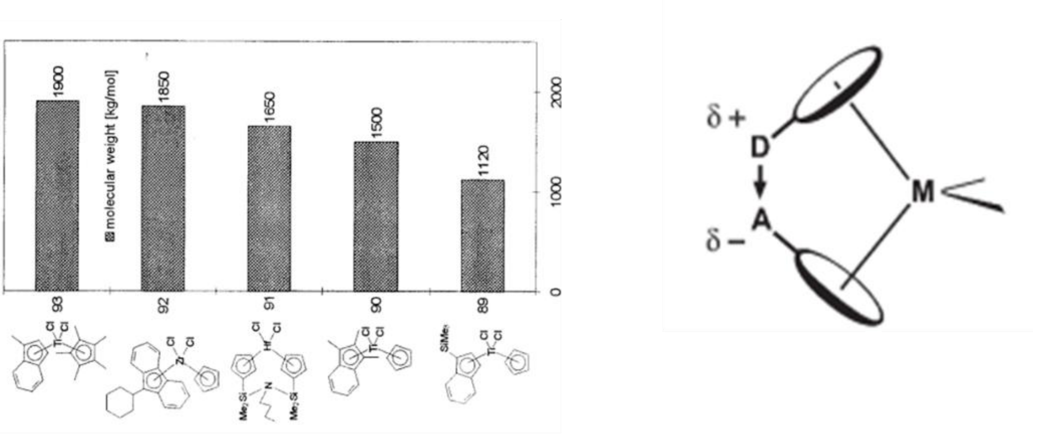
Alt and Köppl reported that complexes with bulky side groups, such as 89, 90, 92, and 93, produced UHMWPE, whereas complex 91, with less bulky ligands but a hafnium center, also produced UHMWPE. The molecular weights of the resulting polymers ranged from 1 to 2 $\times 10^6$ g/mol, as shown in Figure 3a [29].

IImuta and colleagues utilized a catalyst system consisting of ethylene bis(indenyl) hafnium dichloride as the primary catalyst and aluminoxane as the cocatalyst [30]. They employed an ethylene-bridged bis(indenyl) hafnium catalyst to produce high molecular weight copolymers, including UHMWPE, within this study. Copolymerization of ethylene-propylene and ethylene-octene was performed at temperatures ranging from 40 to 90°C under atmospheric pressure. The success of the catalyst is attributed to the “shorter ligand-metal distances, resulting in lower Lewis acidities for hafnium metallocene compared to zirconium analogues, which suppresses chain transfer by β-hydride elimination” [30].

Starjewski and colleagues investigated four zirconocene compounds with donor-acceptor groups attached to each ligand to modulate steric hindrance, as in Figure 3b [31]. They utilized dimethylphosphino or diethylphosphino groups as donors and dichloroboranyl, di-pentafluoroanilineboranyl, or diphenylboranyl as acceptor groups. Two of these compounds, featuring fluorenyl+cyclopentadienyl ligands (Cat-3 and Cat-4) with di-pentafluoroanilineboranyl + diethylphosphino and diphenylboranyl + diethylphosphino acceptor-donor groups, respectively, produced UHMWPE. Unbridged fluorenyl zirconocene catalysts exhibited thermal deactivation, while donor-acceptor bridged compounds (Cat-3 and Cat-4) demonstrated high activity, thermal stability, and UHMWPE production. Additionally, Starjewski and colleagues emphasized the long-chain branching of UHMWPE obtained with Catalysts 3 and 4. Finally, they observed that the molecular weight distributions of the UHMWPE samples became broader with increasing polymerization temperature [31].

3.2. Constrained Geometry Catalyst

Constrained geometry catalysts (CGCs) are developed based on the metallocene breakthrough in olefin polymerization technology. They are founded on the ligand structure first utilized in Bercaw’s organoscandium complex for olefin polymerization catalysts, incorporating cyclopentadienyl-amido ligands [32]. Due to their cyclopentadienyl ligand, they are sometimes referred to as "half metallocene" or "half sandwich" catalysts [33, 34]. CGCs are predominantly employed for the copolymerization of larger α-olefins such as 1-hexene or 1-octene. In comparison to many metallocene complexes, CGCs are thermally stable and capable of producing high molecular weight polymers up to 160°C, albeit with a decrease in molecular weight with increasing temperature [32]. Furthermore, compared to conventional Ziegler-Natta catalysts and metallocene catalysts, CGCs yield ethylene polymers with higher long-chain branching [8]. Commercially, Dow Chemical Company has developed its own platform of constrained geometry catalysts known as INSITE™ catalyst technology [7, 8]. This platform is versatile



(a) (b)

Figure 3. (a) Metallocene complexes produced UHMWPE (Reprinted from Chem. Rev. 2000, 100, 1205−1221 with permission of American Chemical Society) [29]; (b) Donor-Acceptor bridge on metallocene compound (Reprinted from Angew. Chem. Int. Ed. 2006, 45, 1799 −1803 with permission of John Wiley and Sons) [31].

and can be readily modified with fluorenyl or indenyl moieties, as depicted in Figure 4 [35].

In 2000, Chum and colleagues provided a comprehensive summary of this technology in a review paper [7]. However, this review did not focus on or include UHMWPE synthesis [7]. Similarly, in 2008, Chum and Swogger conducted a review that encompassed studies conducted at Dow Chemical Company, including those related to INSITE catalyst technology. However, UHMWPE was not reviewed, as it is not included in Dow Chemical Company's portfolio [8].

In 2006, Hasebe and colleagues investigated INSITE constrained geometry catalysts (CGCs) to produce UHMWPE homopolymers (runs 1 to 4) and ethylene-1-hexene copolymers (runs 5 to 8) [36]. They employed Tebbe Reagent to initiate the reaction, suppress chain transfer to excess hydrogen in the pre-catalyst, and control molecular weight. The reactions were conducted in a continuous stirred-tank reactor (CSTR) slurry reaction. As homopolymers, they obtained four UHMWPE samples ranging from 2 ×10^6 g/mol to 11 ×10^6 g/mol. Hasebe and colleagues employed four different concentrations (0.013, 0.038, 0.13, and 0.38 mmol/h) for the homopolymerization of ethylene. They observed that increasing the concentration of the Tebbe Reagent led to an increase in the molecular weight of the UHMWPE sample, while the crystallinity and density decreased with increasing molecular weight. Additionally, Hasebe and colleagues conducted four ethylene-1-hexene copolymerization trials with varying Tebbe Reagent feed rates (0.045, 0.075, 0.1, and 0.15 mmol/h) and three different 1-hexene feed rates (0.35, 1.1, and 1.8 l/h). They concluded that for homopolymers, increasing the Tebbe Reagent feed rate increased the molecular weight. Conversely, for copolymers, the copolymer feed rate also played a role in controlling chain transfer and thus molecular weight [36].

In 2011, Woo and Hong conducted a comparative study of homogeneous constrained geometry catalysts (CGCs), homogeneous phenoxy-imine (FI) catalysts, SiO_2-supported CGCs, and SiO_2-supported FI catalysts for UHMWPE polymerization [37]. They synthesized CGCs and FI catalysts based on procedures available in the polyolefin catalyst literature, followed by supporting CGCs and FI catalysts on SiO_2 using the same method. Initially, Woo and Hong employed homogeneous CGCs and FI catalysts to produce UHMWPE. Under reaction conditions of 1 bar and 50°C, CGCs failed to produce UHMWPE in both heptane and toluene solvents. Conversely, homogeneous FI catalysts successfully produced UHMWPE when initiated with $Ph_3CB(C_6F_5)_4$. Additionally, homogeneous FI catalysts produced high molecular weight polyethylene when initiated with MAO, although their molecular weights were less than 1 ×10^6 g/mol [37].

In addition, they investigated the use of hexane and toluene as reaction media for the homogeneous FI catalyst [37]. The activity observed in hexane was notably low. Woo and Hong attributed this to the lower solubility of the catalyst and ethylene in hexane, an aliphatic and non-polar solvent, compared to toluene, which is aromatic and relatively more polar, resulting in reduced activity in hexane. A total of 10 polymerization runs were conducted for both homogeneous CGC and FI catalysts to produce UHMWPE. Furthermore, Woo and Hong examined the performance of supported CGC and FI catalysts under various conditions. Fifteen polymerization runs were carried out for SiO_2-supported CGC and FI catalysts to produce

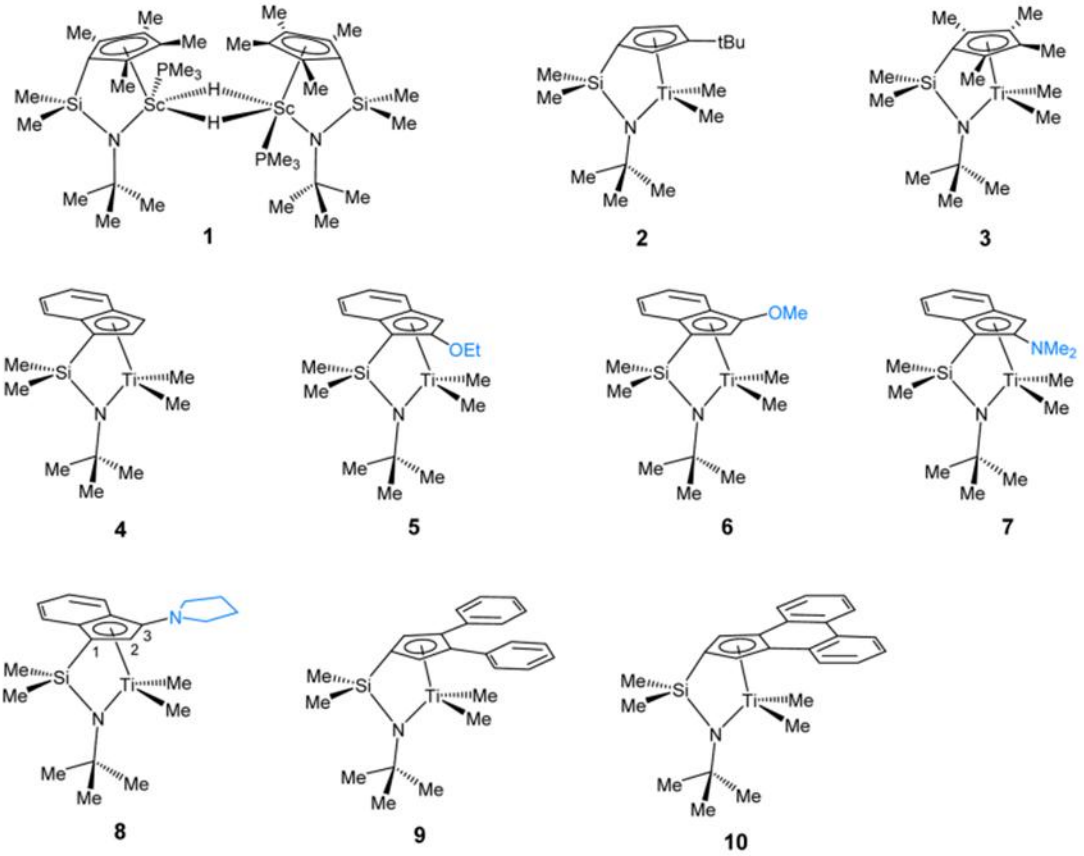


Figure 4. Constrained geometry catalysts with different ligands (Reprinted from Acc. Chem. Res. 2015, 48, 2004–2016 with permission of American Chemical Society) [35]

UHMWPE. For CGC, it was found that increasing the catalyst, monomer, and co-catalyst concentrations enabled the production of UHMWPE with THA and TIBAL. As for the FI catalyst, the effect of co-catalysts was explored by comparing TIBAL, TEAL, and TOA at the same mass (150 mg); however, none of the samples produced UHMWPE, although TIBAL yielded the highest molecular weight among the three co-catalysts [37].

Finally, for the supported FI catalyst, the effects of temperature, monomer concentration, solvents, and Ti concentration were explored, and only one out of six experiments yielded UHMWPE [37]. This particular experiment utilized toluene as the medium, lower temperature (40°C), atmospheric monomer concentration (1 bar), and a higher Ti load (55 μg Ti/g cat). Woo and Hong discussed the molecular weight of UHMWPE concerning propagation and termination steps. They referenced the propagation and termination equations from Rytter and coworkers, Brauseth et al, including the propagation rate, β-hydride elimination to metal, β-hydride elimination to coordinating monomer, and chain transfer to aluminum alkyls [38].

$$\frac{1}{M_n} = \frac{r_1}{r_p} = \frac{K_\beta}{K_p[M]} + \frac{K_M}{K_p} + \frac{K_{Al}[Al]}{K_p[M]} \qquad (1)$$

Equation1: Equation for determining expected molecular weight of UHMWPE (Reprinted from Journal of Polymer Science, Part A: Polymer Chemistry 2005, 43, 2584–2597 with permission of John Wiley and Sons) [37].

In 2018, Severn and coworkers studied the in-situ, bimodal synthesis of UHMWPE using the $MgCl_2$-supported Cp*(tBu_3PN)$TiCl_2$ complex in the presence of TEAL and TIBAL co-catalysts [39]. They obtained different particle-sized catalysts ranging from 1.5 to 12 μm. This study was one of the first examples of a CGC/process combination attempting to produce in-situ UHMWPE particles [26].

In 2020, O'Hare and coworkers synthesized nine derivatives of Me_2SB(tBuN,I*)$TiCl_2$ homogeneous CGC catalysts, which were then supported on solid polymethylaluminoxane (sMAO) [39]. sMAO is insoluble in many common organic solvents. These nine complexes were experimented with in ethylene homopolymerization, ethylene-1-hexene copolymerization, and ethylene-styrene copolymerization in a hexane slurry [39]. For the homopolymerization of ethylene, they obtained UHMWPE with the sMAO-Me_2SB(n-BuN,I*)$TiCl_2$ and sMAO-$Me_2SB(i\text{-}PrN,I^*)TiCl_2$ catalysts. The polymerization conditions were 10 mg catalyst, 2 bar ethylene, 50 mL hexane, 150 mg TiBAL, and 30 min. [39].

For the copolymerization of ethylene with 1-hexene, they conducted both homopolymerization and 1-hexene copolymerization experiments with the sMAO-$Me_2SB(tBuN,I^*)TiCl_2$ catalyst under the same polymerization conditions as described above [39]. For homopolymerization, they obtained UHMWPE at 30^0C, 40^0C, 50^0C, and 60^0C with molecular weights of 2.31 $\times10^6$, 2.20 $\times10^6$, 1.18 $\times10^6$, and 1.06 $\times10^6$ g/mol, respectively. It's noteworthy that they could not obtain UHMWPE with this catalyst before. For copolymerization, at 30^0C with 0.156 mL of 1-hexene, they obtained a molecular weight of 1.29 $\times10^6$ g/mol only. At the same temperature, the molecular weight reduced to 8.56 $\times10^5$ g/mol when the amount of 1-hexene was increased to 0.312 mL. Similarly, at 40^0C with 0.312 mL of 1-hexene, they obtained a molecular weight of 1.13 $\times10^6$ g/mol, which decreased to 7.81 $\times10^5$ g/mol at 40^0C. This reduction in molecular weight is explained by higher chain termination and chain transfer to 1-hexene with the addition of 1-hexene [39].

3.3. Post-Metallocene Catalysts

3.3.1 Phenoxy-imine catalysts

Towards the end of the 1990s, there was significant interest in post-metallocene catalysts, encompassing both early transition metal centered and late transition metal centered catalysts. Brookhart and colleagues, Domski et al, focused on designing ligands and late transition metal centered catalysts, particularly Ni and Pd, for olefin polymerization [40]. Concurrently, Fujita and colleagues directed their attention to ligand design and early transition metal centered catalysts, especially Ti and Zr. Although both groups studied phenoxy-imine ligands, Fujita and colleagues achieved notable advancements in polymerization [41].

Fujita and colleagues at Mitsui Chemicals pursued a ligand-oriented design approach while investigating phenoxy-imine type catalysts [10]. In addition to phenoxy-imine catalysts (FI), they synthesized indolide-imine (II) catalysts, pyrrolide-imine (PI) catalysts, imine-phenoxy (IF) catalysts, and phenoxy-ether (FE) ligated Ti complexes. Beyond group 4 transition metal complexes, they also synthesized imine-pyridine ligated Ni complexes (IP catalysts) and tris(pyrazolyl)borate ligated Ta complexes (PB catalysts) [10].

Within the research on phenoxy-imine ligands, tridentate (ONN, ONO) and tetradentate phenoxy-mine complexes (ONNO), particularly titanium-centered phenoxy-imine catalysts with fluorophenyl substituents, have demonstrated "living polymerization" properties for ethylene and propylene under atmospheric pressure and moderate temperatures [42]. “An active species for the living polymerization is stable for at least 1 hour at room temperature even without ethylene monomers, which allows room-temperature observation of the living propagating species” [9]. Unlike metallocene and constrained geometry catalysts, FI catalysts form octahedral complexes as given in Figure 5 [9].

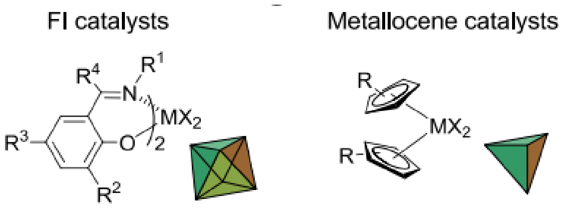


Figure 5. Tetrahedral and octahedral structures of metallocene and FI catalysts (Reprinted from Top Catal (2014) 57:852–877 with permission of Springer Nature) [9].

Fujita and coworkers compared the electrophilic natures of the metallecone, CGC and FI catalysts, as in Figure 6, and concluded “Due to the coordination of heteroatom-based [O-, N-] ligands, which are more electron-withdrawing than Cp-based ligands, the catalytically active species originating from FI catalysts exhibit a highly electrophilic nature compared to those derived from metallocene catalysts” [9].

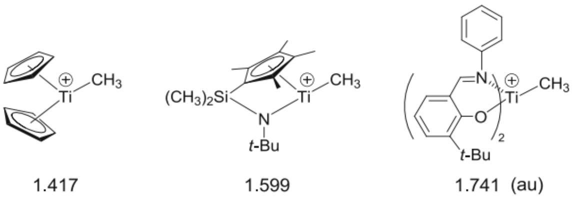


Figure 6. Milliken charges of central titanium ions in metallocene, CGC and FI catalysts (Reprinted from Top Catal (2014) 57:852–877 with permission of Springer Nature) [9].

One of the most significant characteristics of FI catalysts is that ortho-fluorinated FI catalysts, when combined with MAO, can mediate highly controlled, thermally robust living polymerizations of ethylene. When comparing the seven fluorinated FI complexes shown in Figure 7, it was observed that the ortho-fluorinated complexes (complexes 6, 7, 8, and 9) successfully conducted living polymerization of ethylene. Conversely, the non-ortho-fluorinated (complexes 10 and 11) and ortho-methylated (complex 12) Ti–FI catalysts did not facilitate living

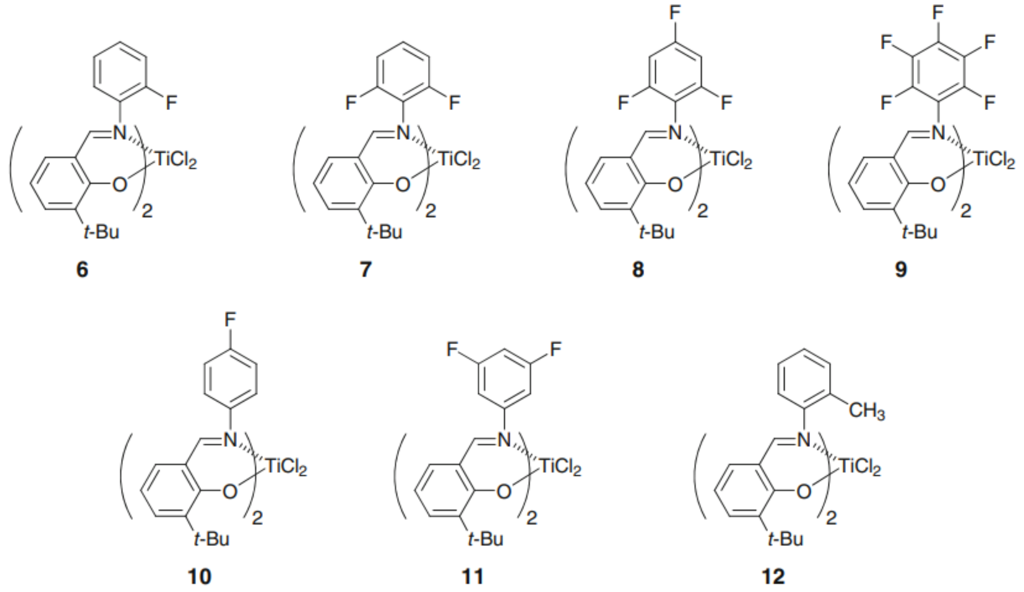


Figure 7. Phenoxy-imine catalysts with differentiating fluorophenyl groups (Reprinted from Top Catal (2014) 57:852–877 with permission of Springer Nature) [9].

polymerization under identical conditions. It was concluded that the ortho-fluorine substituents may influence the living polymerization electronically rather than sterically [9].

Based on experimental studies and DFT calculations, as submitted in Table 4, Kawai and Fujita concluded that “the unprecedented living polymerization induced by ortho-fluorinated Ti–FI catalysts in combination with MAO originates from an attractive non-bonding interaction between the ortho-F and a β-H on the growing polymer chain. This interaction (calculated F/H distances of 2.2–2.4 Å, modeled on a cationic n-propyl species) stabilizes the chain against β-hydrogen transfer, the predominant chain termination mechanism, as shown in Figure 8. It is important to note that the calculated ortho-F/Ti distances range from 3.6 to 3.9 Å, indicating minimal interaction between the cationic metal center and the ortho-F, likely due to the relatively rigid catalyst framework.” [9]. Furthermore, Kawai and Fujita reported that the alkyl substituents ortho to the phenoxy-Os, which are positioned above and below the active sites, play a crucial role in monomer selectivity. They observed that an increase in the steric bulk of these alkyl substituents generally leads to enhanced selectivity for ethylene over α-olefins. This finding is significant for the synthesis of UHMWPE homopolymers and copolymers [9].

“Regarding ultra-high molecular weight polyethylenes (PEs), the Zr–FI catalysts described exhibit exceptionally high ethylene selectivity when used with either $MgCl_2/RO_nAl(OR)_{3-n}$ or SiO_2-supported MAO, a common support for metallocene catalysts. These catalysts are capable of polymerizing ethylene to produce ultra-high molecular weight PEs with good morphology, as in Figure 9, and virtually no branching, resulting in truly linear PEs. This is in stark contrast to heterogeneous Ziegler/Natta catalysts, which typically yield PEs with 0.3–0.6 methyl branches per 1,000 carbons during ethylene homopolymerization ” [9].

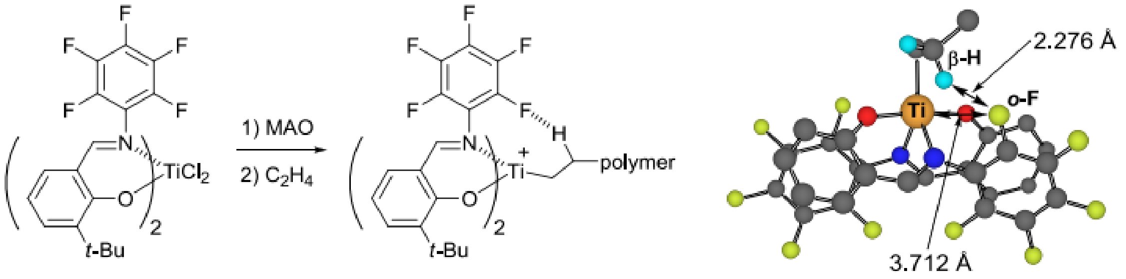
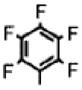
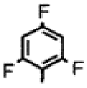


Figure 8. Calculated structure of a cationic n-propyl species derived from FI catalyst (Reprinted from Top Catal (2014) 57:852–877 with permission of Springer Nature)[9].

Table 4. DFT calculation results of F-H$_β$ interactions (Reprinted from 3328 J. Am. Chem. Soc. 9 Vol. 124, No. 13, 2002 with permission of American Chemical Society) [42].

-R				
Complex no:	**1**	**2**	**3**	**4**
r(F-H$_β$)^a	2279	2362	2346	2324
q(F)^b	-0.466	-0.470	-0.476	-0.482
q(H$_β$)^c	0.095	0.108	0.111	0.117
ES(F-H$_β$)^d	-27.1	-29.9	-31.2	-33.9

a) (F-H$_β$) distance (Ā) b) Mulliken charge of the nearest o-F to H$_β$ c) Mulliken charge of H$_β$
d) Electrostatic energy for (F-Hβ) interaction (kJ/mol).

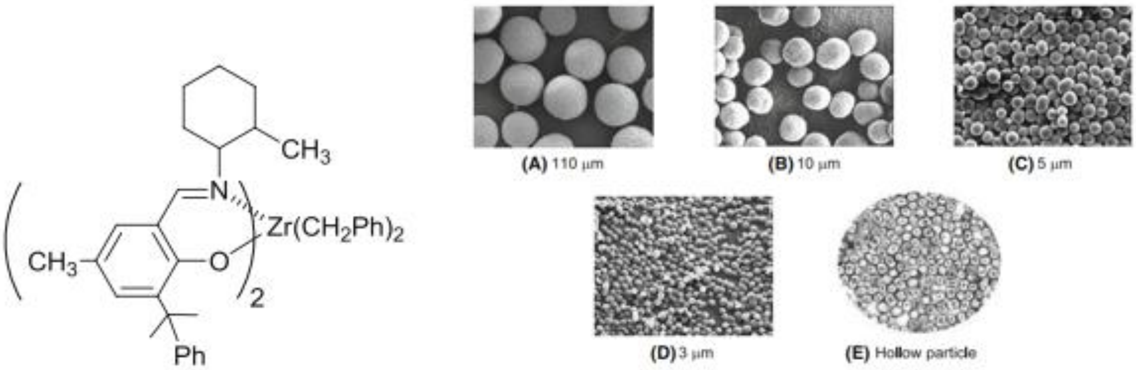


Figure 9. Zr - FI catalyst with very high ethylene selectivity (Reprinted from Top Catal (2014) 57:852–877 with permission of Springer Nature) [9].

The entanglement of UHMWPE plays a crucial role in fiber performance. Werf and Heisserer elucidate the relationship between entanglement and fiber performance, stating, "Due to the reduction in the number of entanglements per polymer chain, which results from dissolution and the low interaction between polyethylene chains, very high draw ratios can be achieved. This leads to extremely high molecular orientation and consequently, high fiber strength and modulus" [43].

The FI catalyst facilitates the production of nascent disentangled UHMWPE, where the entanglement density is significantly lower than that of conventional UHMWPE. Christakoupulos explains, "Due to the slow reptation time associated with UHMWPE owing to its high molecular weight, the number of entanglements is high, approximately 1250 g/mol (ca. 2400 entanglements per chain). In contrast, the synthesis of disentangled UHMWPE (dUHMWPE) using phenoxy-imine catalysts results in a reduced entanglement count, ranging from 100 to 200 entanglements per chain" [44, 45].

The synthesis of disentangled UHMWPE is predicated on achieving a rapid crystallization rate that exceeds the polymerization rate, which allows the growing polymer chain to crystallize swiftly [46]. This rapid crystallization reduces the likelihood of self-entanglement or entanglement with neighboring chains. Employing homogeneous catalysts, as opposed to heterogeneous ones, further diminishes the probability of entanglement due to the effective dispersion of active sites—and consequently the growing chains—within the reaction medium [9][46].

Rastogi and colleagues conducted further research on UHMWPE synthesis and the entanglement of polymer chains using a pentafluorophenyl-substituted FI catalyst, [(3-tert-butylsalicylidene) pentafluoroanilinato titanium(IV). Their objective was to utilize a homogeneous FI catalyst to regulate the proximity of active centers and the crystallization of polymer chains growing on these active centers [46-49].

In 2011, Rastogi and colleagues investigated the entanglement of UHMWPE samples synthesized by an FI catalyst and a commercial UHMWPE fiber, Dyneema SK75, produced with a conventional Ziegler-Natta catalyst. They characterized the samples using SEM, tensile testing, XRD, and dynamic NMR studies. SEM images of UHMWPE samples obtained with the FI catalyst, showing low entanglements, and those obtained with the Ziegler

Natta catalyst, showing high entanglements, are presented in Figure 10 [47].

They concluded that the samples obtained with the Ziegler-Natta catalyst and the FI catalyst can be distinguished based on the chain diffusion process and topological constraints with solid-state NMR. Disentangled UHMWPE can be drawn in a much broader temperature window compared to conventional UHMWPE. Additionally, its tensile properties are better than those of solvent-drawn UHMWPE [47].

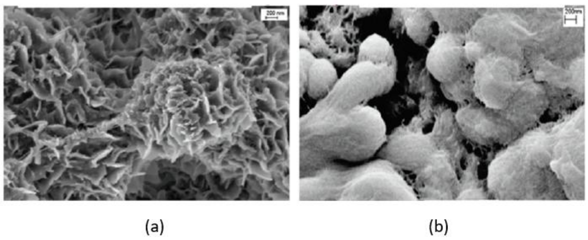


Figure 10. UHMWPE samples having a) low entanglements and b) high entanglements (Reprinted from Macromolecules 2011, 44, 5558–5568 with permission of American Chemical Society) [47].

In 2012, Rastogi and co-workers studied the effect of two different co-catalyst types on UHMWPE polymerization and entanglement. They utilized standard MAO and Butylated hydroxytoluene, BHT-modified MAO for the polymerization of ethylene with the FI catalyst. Following polymerization, the polymers obtained with the two different FI-MAO catalyst/co-catalyst systems were characterized morphologically using SEM, thermally with DSC, and rheologically with a strain-controlled rheometer. For polymerization, they employed co-catalyst ratios of 0, 0.3, 0.45, and 0.6 mol/mol of BHT/MAO. The polymerization results obtained are tabulated in Table 5 [48].

Rastogi and co-workers concluded that BHT trapping TMA in MAO aids in achieving higher catalytic activity. With standard MAO, a form of catalytic deactivation occurs due to TMA. Additionally, the UHMWPE samples obtained with the FI+BHT/MAO catalytic systems exhibit much lower entanglement density compared to commercial UHMWPE samples. Entanglement density was calculated using the Ferry Equation [48].

In 2013, Rastogi and coworkers conducted a variation of the aforementioned study, maintaining a fixed BHT/MAO ratio while varying the reaction times [49]. Other reaction conditions remained unchanged. They examined polymerization times ranging from 2 minutes to 60 minutes and obtained polyethylene samples with molecular weights ranging from 0.6 ×10^6 g/mol to 9 ×10^6 g/mol. The results of the study are provided in Table 6 [49].

Based on the difference in molecular weights observed between the PE samples with MAO co-catalyst and those with MAO+BHT co-catalyst, they concluded that the main active catalytic species are consistent between MAO and MAO+BHT co-catalysts. However, they noted that the secondary catalytic species differ [49]. In the presence of MAO alone, where TMA substituents are present, the catalytic species formed exhibit a higher propensity for producing higher molecular weight PEs [49]. This conclusion contradicted the findings of the 2012 study [48].

In 2015, Rastogi and colleagues investigated the impact of various types of MAO co-catalysts and activation times on polymerization with the FI catalyst. They employed methyl aluminoxane (MAO), polymethyl aluminoxane (PMAO), and modified methyl aluminoxane-12 (MMAO-12) as co-catalysts. Additionally, they utilized BHT as a catalyst modifier with MAO, as in previous studies [46].

From the polymerization data presented in Table 7 for MAO and MAO+BHT co-catalysts, Rastogi and colleagues observed that catalyst activity is dependent on the activation time. When MAO is used without a catalyst modifier, catalytic activity decreased by up to 65% after 30 minutes of activation time. However, when MAO is used with a catalyst modifier (0.2 g of BHT), the decrease in catalytic activity was around 10% after 30 minutes of activation time. They attributed the reduction in catalytic activity with MAO only to several factors: i) possible formation of dimethyl bridged species between TMA and the catalyst leading to the formation of dormant sites, ii) reduction of Ti(IV) into Ti(III), and iii) ligand transfer from the catalyst to TMA [46].

Rastogi and colleagues also investigated the polymerization of ethylene using PMAO and MMAO-12 as co-catalysts. They observed that the catalytic activity of the FI catalyst with PMAO or MMAO-12 was generally lower compared to MAO and MAO+BHT. However, contrary to activation with MAO, increasing the activation time with PMAO and MMAO-12 resulted in an increase in the catalytic activity of the FI catalyst as in Table 8. Rastogi and colleagues attributed this difference to the slower rate of activation or lower capability of activation of PMAO and MMAO-12 compared to MAO. Additionally, the difference in the content and type of TMA in PMAO and MMAO-12 was considered as another influencing factor [46].

Due to their ability to sustain living ethylene polymerization, catalysts featuring ortho-fluorophenyl and pentafluorophenyl on the imine

Table 5. BHT/MAO ratios and polymerization yields of ethylene polymerization experiments. (Reprinted from Advances in Polymer Technology, 31(3) 193-204 (2012) with permission of John Wiley and Sons) [48].

Sample	BHT/MAO (mol/mol)	Rp kg/(mol h bar)
PE1	0	2823
PE2	0.3	3126
PE2 bis	0.3	3214
PE3	0.45	4616
PE3 bis	0.45	4514
PE4	0.6	4869
PE4 bis	0.6	4930

Other reaction conditions: FI catalyst: 6.2 μmol; MAO: 7.5 mmol; MAO/Ti ratio: 1200; solvent, 0.75 L toluene; Temperature, 10 °C; ethylene pressure, 1.1 bar; reaction time, 60 min.

Table 6. Ethylene polymerization runs with and without BHT modifier (Reprinted from Journal of Polymer Science, Part A: Polymer Chemistry 2013, 51, 1630–1635 with permission of John Wiley and Sons) [49].

Run	Polymerization Time (min)	Cocatalyst	Yield (g)	Rp (kg$_{PE}$/mol$_{cat}$ atm h)	Mw x 10^6 (g/mol)	Mn x 10^6 (g/mol)	MWD
1	2	MAO	2.0	8.764	0.7	0.5	1.3
2	2	MAO+BHT	3.2	13.748	0.6	0.5	1.2
3	10	MAO	8.1	6.96	2.3	1.2	1.9
4	10	MAO+BHT	9.3	8.151	1.8	1.0	1.8
5	30	MAO	17.3	4.955	5.6	1.8	3.2
6	30	MAO+BHT	20.6	6.018	4.2	1.8	2.4
7	60	MAO	28.4	3.989	9.0	2.6	3.4
8	60	MAO+BHT	35.1	4.93	7.2	2.7	2.7

Other conditions: temperature=10^0C; ethylene pressure=1,1 bar; catalyst=6.2 μmol; Al/Ti=1,200; toluene=0.75 L.

side, and a single bulky alkyl group on the ortho-position of the phenoxy side, have become benchmark complexes for researchers studying ethylene polymerization, especially UHMWPE [1,9, 10]. In parallel, many variants based on this "gold standard" complex have been investigated. Considering the steric and electronic effects of the ligands, as well as the molecular structures and moieties attached to these ligands, is crucial for this research. For example, attaching larger pendant groups, different kinds of halides, or pendant atoms or groups to the meta or para positions of the phenyl group is extensively explored. Additionally, variations such as bridging phenoxy-imine groups with varying sizes and lengths to obtain single tetradentate ligands, or bridging the phenoxy-imine ligands with another metal center, are also studied [1,9,10, 54].

In 2010, Jones and colleagues conducted a study on three catalysts, building on the research of Fujita and co-workers [50]. Complexes (a) and (b) had been previously investigated, and the polymerization results were documented in the literature. Building upon these two known complexes, Jones and colleagues synthesized a hybrid complex (c), as presented in Table 9. They compared the results of UHMWPE synthesis using this hybrid complex with those obtained using a $TiCl_3$ Ziegler-Natta catalyst and a Mg/Si (Sylopol) supported Ziegler-Natta catalyst. Jones and coworkers concluded that the reactivities of supported Ziegler-Natta catalysts are higher at commercially relevant temperatures and pressures [50].

In 2012, Damavandi and coworkers replaced the metal center from Ti to Zr and altered the ligand from salicylaldehyde to 2-hydroxynaphthaldehyde, transforming the catalyst into a naphthoxy-imine catalyst [51]. Initially, they synthesized Bis[1-[(2,6-diisopropylphenyl)imino]methyl-2-naphtholato] zirconium(IV)dichloride, but its activity was found to be unsatisfactory by the researchers. As an alternative, they synthesized Bis[1-[(2′,6′-diisopropylphenyl)imino]methyl-3,6-ditert-butyl-2-naphtholato]zirconium(IV) dichloride, and its activity was found to be quite satisfactory. The researchers obtained UHMWPE using this catalyst with a MAO activator. Damavandi and coworkers obtained UHMWPE samples with Mv ranging from 0.88×10^6 g/mol to 2.91×10^6 g/mol in different polymerization runs [51].

In 2023, Li et al studied Titanium Complexes Bearing Nonsymmetric Amine-bis(phenolate) Ligands" for the synthesis of UHMWPE. As a subset of ONNO type tetradentate ligands, they synthesized seven different Ti complexes with amine-bisphenolate ligands, as depicted in Figure 11 [52]. At a reaction temperature of 40°C, they synthesized UHMWPE using complexes 3, 4, 5, 6, and 7, with complex 7 yielding the highest molecular weight UHMWPE among the tested complexes. Additionally, they successfully synthesized UHMWPE samples using complex 7 at 80°C, but not at 120°C. The results of the ethylenepolymerization runs are tabulated in Table 10 [52].

In 2023, Tuskaev and colleagues investigated

Table 7. Ethylene polymerization data using MAO and in combination with a co-catalyst modifier in different activation procedures (Reprinted from Macromol. Symp. 2015, 356, 61–69with permission of John Wiley and Sons) [46].

Run	Co-catalyst as scavenger	Co-catalyst as activator	Activation time [min]	Rp^a	M_w [10^6 g/mol]	MWD
1	4 ml of MAO	1 ml of MAO	0	4000	9.3	3.3
2	4 ml of MAO	1 ml of MAO	15	2650	11.2	7.8
3	4 ml of MAO	1 ml of MAO	30	1450	nd	nd
4	4 ml of MAO	1 ml of MAO+0.2 g of BHT	0	4150	7.5	3.7
5	4 ml of MAO	1 ml of MAO+ 0.2 g of BHT	15	4200	7.1	3.5
6	4 ml of MAO	1 ml of MAO+0.2 g of BHT	30	3700	6.6	3.5
7	4 ml of MAO + 0.8 g of BHT	1 ml of MAO+ 0.2 g of BHT	0	4950	7.8	3.3

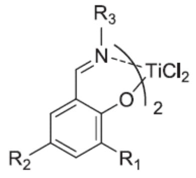
Other conditions: Al/Ti molar ratio, 1200; catalyst, 6.2 ± 0.2 mmol; temperature, 10 °C; reaction volume, 750 ml of toluene; reaction time, 60 min; ethylene pressure, 1.1 atm. ^{a}kg$_{PE}$/mol$_{Ti}$*atm*hour.

Table 8. Ethylene polymerization data with PMAO and MMAO-12 with varying activation times (Reprinted from Macromol. Symp. 2015, 356, 61–69with permission of John Wiley and Sons) [46].

Run	Co-catalyst	Activation time [min]	Rp^a
8	PMAO	0	900
9	PMAO	10	2850
10	PMAO	30	2200
11	MMAO12	0	1150
12	MMAO12	10	2500
13	MMAO12	30	3000

Other conditions: Al/Ti molar ratio, 1850; catalyst, 6.2 ± 0.2 mmol; temperature, 10 ^{0}C; reaction volume, 750 ml of toluene; reaction time, 60 min; ethylene pressure, 1.1 atm. a kgPE/molTi*atm*hour.

Table 9. Ethylene polymerization catalysts, base complex (a) and base complex (b) and hybrid complex (c) [48].



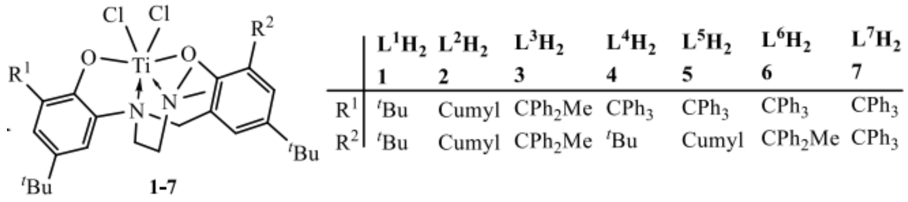
	Base Complex (a)	Base Complex (b)	Hybrid Complex (c)
R_1	I	isobutyl	I (a)
R_2	I	H	I (a)
R_3	2-6 difluorophenyl	heptyl	heptyl (b)

complexes with fluorinated and non-fluorinated aliphatic phenoxyimine ligands and a titanium center [53]. They synthesized 10 different complexes, as listed in Table 11, and utilized various activators, namely MMAO-12, $Et_2AlCl+Bu_2Mg$, and $Et_3Al_2Cl_3+Bu_2Mg$, for polymerization. Their findings indicated that the complexes activated with $Et_3Al_2Cl_3+Bu_2Mg$, which exhibits higher Lewis acidity than $Et_2AlCl+Bu_2Mg$, outperformed those activated with $Et_2AlCl+Bu_2Mg$ and MMAO-12. Additionally, complexes containing fluorine atoms exhibited lower productivity with MMAO-12 but yielded high molecular weight polymers. Another significant observation pertained to the morphology of the UHMWPE obtained with MMAO-12; the samples displayed a characteristic morphology of large lamellar crystals with a "wave-like" shape interconnected by fibrils" [53].

In the literature, numerous studies and publications explore post-metallocene catalysts and UHMWPE synthesis, covering both early transition metal and late transition metal catalysts. One fundamental review concerning FI catalysts and their variants was conducted by Fujita et al. in 2011 [10]. In 2020, Chikkali and colleagues provided a comprehensive review spanning from UHMWPE synthesis to its applications [1]. Additionally, in 2021, Antonov and Bryliakov reviewed post-metallocene catalysts for UHMWPE synthesis, summarizing the "recent advances" in the field [54].

3.3.2 Immobilization of phenoxy-imine catalysts

Supporting homogeneous catalysts has always posed a challenge for both metallocene and non-metallocene catalysts. However, without support, it is not feasible to utilize homogeneous catalysts in commercial UHMWPE reactors. Therefore, immobilizing FI catalysts is a critical step in enabling their use on a commercial scale. In their review paper, Klapper and colleagues explored the support of metallocene catalysts on classical inorganic supports such as SiO_2 and $MgCl_2$, as well as on novel organic nanoparticles including polystyrene or porous polyurethane nanoparticles,



	L^1H_2	L^2H_2	L^3H_2	L^4H_2	L^5H_2	L^6H_2	L^7H_2
	1	2	3	4	5	6	7
R^1	^{t}Bu	Cumyl	CPh_2Me	CPh_3	CPh_3	CPh_3	CPh_3
R^2	^{t}Bu	Cumyl	CPh_2Me	^{t}Bu	Cumyl	CPh_2Me	CPh_3

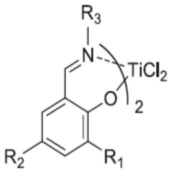
Figure 11. Amine-bis phenolate Ti Complexes used in ethylene polymerization (Reprinted from Macromolecules 2023, 56, 6764–6775 with permission of American Chemical Society) [52].

Table 10. Ethylene polymerization runs conducted with amine-bisphenolate Ti complexes 1 to 7 (Reprinted from Macromolecules 2023, 56, 6764–6775 with permission of American Chemical Society) *[52]*.

Run	Catalyst	Cocatalyst	T (°C)	Yield (g)	Activityb	Mwc	PDIc
1	1	MAO/BHT	40	0.494	0.99	76.3	1.9
2	2	MAO/BHT	40	0.912	1.82	91.5	2.2
3	3	MAO/BHT	40	0.927	1.85	129.6	2.1
4	4	MAO/BHT	40	1.197	2.39	191.4	2.5
5	5	MAO/BHT	40	1.511	3.02	290	2.3
6	6	MAO/BHT	40	1.692	3.38	292.5	2.1
7	7	MAO/BHT	40	1.809	3.62	373.7	1.9
8	7	MAO/BHT	80	1.993	3.98	200.7	2.2
9d	7	MAO/BHT	120	1.647	3.29	89.3	2
10	7	MAO	40	2.142	4.28	41.6	2.7
11	7	dry-MAO	40	1.718	3.44	296.5	1.5
12	7	$AliBu_3/Ph_3CB(C_6F_5)_4$	40	1.773	3.55	286.6	1.7

a- Polymerization conditions: toluene 80 mL; Ti = 1 μmol, MAO/Ti = 1000, dry-MAO/Ti = 1000, AliBu3/Ti = 100, Ph3CB(C6F5)4/Ti = 1.2, time 0.5 h, ethylene pressure 5 bar. b-Units of 106 g (mol Ti)−1 h−1. c-Units of 104 g mol−1, determined by GPC. d- 80 mL of xylene was used instead of toluene.

Table 11. Phenoxyimine Ti complexes synthesized to obtain dUHMWPE *[53]*.

		comp 01	**comp 02**	**comp 03**	**comp 04**	**comp 05**
	Cl or OiPr	Chloride	Chloride	Diisopropylate	Diisopropylate	Chloride
	R_1	tButyl	tButyl	tButyl	tButyl	tButyl
	R_2	tButyl	tButyl	tButyl	tButyl	tButyl
	R_3	isoprpyl	$CH(CF_3)_2$	isoprpyl	$CH(CF_3)_2$	C_7H_{15}
		comp 08	**comp 07**	**comp 08**	**comp 09**	**comp 10**
	Cl or OiPr	Chloride	Diisopropylate	Diisopropylate	Chloride	Diisopropylate
	R_1	tButyl	tButyl	tButyl	tButyl	tButyl
	R_2	tButyl	tButyl	tButyl	tButyl	tButyl
	R_3	$CH_2C_6F_{13}$	C_7H_{15}	$CH_2C_6F_{13}$	C_7H_{15}-C_8H_{17}	C_2H_4-C_8H_{17}

pyridine-functionalized nanoparticles and hollow spheres, non-aqueous emulsions, and electrospun fibers [55]. An example of the immobilization of FI catalysts was provided based on a previous study by Klapper, Fujita, and colleagues, Naundorff et al. They successfully immobilized FI catalysts on nanoscale latex particles composed of a styrene, 4-vinylpyridine, and divinylbenzene terpolymer support [56].

Gagieva et al., in 2019, immobilized the bis-(3,5-di-tert-butylsalicylidene)-2,3,5,6-tetrafluoroaniline titanium(IV) dichloride complex on silica gel, polysorb, and magnesium chloride. They utilized the tetrakis(perfluorophenyl)borate activator $[Me_2NHPh][B(C_6F_5)_4]$ [57]. The aim of the study was to enhance the catalyst's activity by immobilizing the catalyst complex and increasing the molecular weight through the substitution of MAO with tetrakis(perfluorophenyl)borate. Gagieva and colleagues conducted 16 different polymerization runs and compared the activities. They concluded that the FI catalyst supported on magnesium chloride outperforms both its homogeneous analog and those supported on silica gel or polysorb [57].

Table 12. Characteristics of UHMWPE produced with four different catalytic systems (Reprinted Macromolecules 2023, 56, 361−378 with permission of American Chemical Society) [59].

Sr. No	**Catalytic System**	**State of UHMWPE**	**Morphology Control**	**Processing Technique**	**Mechanical Properties (max achieved)**	**Limitation**
1	homogeneous FI/MAO	highly disentangled	no	solid-state (without solvent)	ultimate (4 GPa/200 GPa)	reactor fouling (limits to batch process)
2	heterogeneous Z−N (commercial)	fully entangled	yes	solution spinning (use of 90% carcinogenic solvent)	superior (3.5 GPa/135GPa	highly entangled (not solid-state processable)
3	heterogeneous modified Z−N and FI/MAO	relatively low disentangled	yes	solid-state (without solvent)	limited (2.7 GPa/170 Gpa	limited mechanical properties
4	heterogeneous Cat. 1/$MgCl_x$/Et_nAl_y(2-ethyl-1-hexoxide) [59]	highly disentangled	yes	solid-state (without solvent)	ultimate (4 GPa/200 GPa)	no limitations of cat.1

Rastogi and co-workers, in 2023, utilized MgClx/EtnAly (2-ethyl-1-hexoxide), an "in situ formed activator/support," with the bis[N-(3-tert-butylsalicylidene) pentafluoroanilinato] titanium(IV) dichloride catalyst. This activator/support structure is based on the work conducted by Fujita and coworkers in 2006, but they modified the preparation procedure as detailed in their work [58, 59]. They compared the characteristics of four different catalytic systems for producing UHMWPE, as shown in Table 12 [59].

3. Conclusion

Catalysis plays a crucial role in polyolefin synthesis, and UHMWPE, as a distinct subgroup of polyolefins, presents additional complexities, particularly concerning β-hydrogen chain transfer and temperature stability. Currently, Ziegler-Natta catalysts remain dominant in industry for synthesizing various grades of UHMWPE due to their robust and well-established heterogeneous structure. Titanium-based Ziegler-Natta catalysts offer cost advantages to resin manufacturers, with their alkyl aluminum co-catalysts readily available from multiple global suppliers at relatively low costs. Given the diverse processing methods, Ziegler-Natta UHMWPE is poised to continue dominating the market in the near future. Metallocene and half-metallocene catalysts are also employed in UHMWPE synthesis, with unique half-metallocene Titanium complexes, originally developed for linear low-density polyethylene (LLDPE) synthesis, proving successful for UHMWPE production due to their superior temperature stability. Although metallocene and post-metallocene catalysts are not extensively used for UHMWPE synthesis, they have contributed significantly to the development of post-metallocene catalysts. Fine-tuning the electronic and steric properties of catalysts through "ligand-based design" has emerged as a key concept, inspired by achievements in metallocene catalysts. In the late 1990s, Fujita and researchers at Mitsui Chemicals introduced the Phenoxy-Imine (FI) catalyst family, which has demonstrated excellent polymerization performance for both ethylene homopolymerization and copolymerization with higher alpha olefins. Ortho-fluorinated FI catalysts, when initiated with methylaluminoxane (MAO), can exhibit prolonged "living polymerization" conditions, offering an advantage in UHMWPE synthesis. UHMWPE synthesized with homogeneous FI catalysts, such as (3-tert-butylsalicylidene) pentafluoroanilinato titanium (IV), exhibits lower entanglement density compared to its Ziegler-Natta counterpart, earning designations like "disentangled UHMWPE" or "dUHMWPE" in literature and industry. This lower entanglement density allows solid-state processing of UHMWPE, offering new opportunities for applications such as additive manufacturing using 3D printers. While homogeneous FI catalysts are applicable for UHMWPE synthesis, reactor fouling remains a challenge for large-scale production. Hence, many researchers are investigating the immobilization of FI catalysts or their variants, with Mg_2Cl being the most widely used support due to its high compatibility, industrial applicability, and feasibility. Additionally, nanoscale organic supports, with defined support geometries, represent an emerging and intriguing area of research within the polyolefin catalyst domain.

Authors' Contributions:

EK: Conceptualization, Methodology, Data curation, Writing- Original Draft, Visualization.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Conflict of Interest

There is no conflict of interest in this study.

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