Materials Technology Reports 2025, 3(1), 3164.
https://doi.org/10.59400/mtr3164

Review

Catalytic strategies for synthesizing disentangled ultrahigh molecular weight polyethylene via homogeneous FI catalyst-based polymerization

Lei Li[1,2,3]

[1] SINOPEC Nanjing Research Institute of Chemical Industry Co., Ltd., Nanjing 210048, China; lionel93@sina.com
[2] China Petroleum and Chemical Corporation, Beijing 100728, China
[3] Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

CITATION

Li L. Catalytic strategies for synthesizing disentangled ultrahigh molecular weight polyethylene via homogeneous FI catalyst-based polymerization. Materials Technology Reports. 2025; 3(1): 3164.
https://doi.org/10.59400/mtr3164

ARTICLE INFO

Received: 24 April 2025
Accepted: 13 May 2025
Available online: 3 June 2025

Abstract: Ultrahigh molecular weight polyethylene (UHMWPE) is a high-performance polymer renowned for its exceptional mechanical strength, wear resistance, and chemical stability, making it indispensable in medical, industrial, and protective applications. However, its highly entangled molecular structure severely limits processability due to its extreme melt viscosity. Recent advancements in homogeneous catalyst-based polymerization, particularly using bis(phenoxyimine) titanium (FI) catalysts, have enabled the synthesis of disentangled UHMWPE (dis-UHMWPE), offering a breakthrough in overcoming these challenges. FI catalysts exhibit unique advantages, including living polymerization behavior, single-site homogeneity, and tunable steric/electronic effects, allowing precise control over molecular weight, narrow polydispersity, and reduced entanglement density. These features facilitate solvent-free solid-state processing, significantly improving melt processability while enhancing mechanical properties compared to conventional Ziegler-Natta (Z-N) catalyst-derived UHMWPE. Notably, key strategies such as low-temperature polymerization, cocatalyst modification, and optimized reaction kinetics when using an FI catalyst further ensure controlled chain propagation and crystallization, minimizing entanglements. This review highlights the transformative potential of FI-catalyzed dis-UHMWPE, including its inherent properties, advantages, and technical implementation details, in the preparation of dis-UHMWPE, setting a new benchmark for sustainable and high-performance polyolefin materials.

Keywords: dis-UHMWPE; FI catalyst; homogeneous catalyst; entanglement; single-site catalysis

1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE), characterized by its extraordinarily high molecular weight (MW) (typically exceeding 1×10^6 g/mol), represents a class of advanced polymeric materials with exceptional mechanical properties [1–3]. This engineering thermoplastic exhibits outstanding wear resistance, remarkable impact strength, and excellent chemical stability, making it indispensable for demanding applications such as orthopedic implants, ballistic protection, high-performance fibers, and industrial liners [4–6]. Particularly noteworthy is its extremely low coefficient of friction and self-lubricating characteristics, which render it an ideal material for artificial acetabular cups in medical devices [7]. In industrial settings, UHMWPE components, including filter plates, gears, and guide rails, demonstrate significantly extended service life under harsh operating conditions compared to conventional polyethylene [8]. In the medical field, UHMWPE fibers are used in artificial joints, orthopedic instruments, and antibacterial sutures due to their

biocompatibility and low density, improving implant quality and reducing infection risk [9–11]. In the military, it relies on an ultra-high strength-to-weight ratio as a lightweight bulletproof material that combines weather resistance and corrosion resistance. The current research is dedicated to interface enhancement and compositing to expand their applications in intelligent protection and biological devices [12–15]. Furthermore, its superior dielectric properties and resistance to environmental stress cracking have enabled widespread applications in cable insulation and chemical processing equipment [16,17]. These outstanding characteristics have established UHMWPE as a focal point in advanced polymer research and development.

Conventional commercial UHMWPE faces significant challenges primarily due to its highly entangled molecular architecture [18,19]. This entangled network results in extremely high melt viscosity (typically > 10^8 Pa·s), rendering standard melt-processing techniques (e.g., injection molding and extrusion) practically infeasible. The current industrial processes predominantly rely on specialized methods like sintering and compression molding, which are not only energy-intensive and inefficient but also limited in producing complex geometries [17,20]. More critically, severe chain entanglements restrict the regular arrangement of polymer chains during crystallization, leading to substantial amorphous regions that compromise the material's ultimate mechanical performance [21,22]. The emergence of disentangled UHMWPE (dis-UHMWPE) offers a promising solution to these limitations [23,24]. By significantly reducing interchain entanglement density, dis-UHMWPE exhibits melt viscosities 2–3 orders of magnitude lower than conventional UHMWPE, significantly improving processability [25,26]. More importantly, during subsequent solid-state processing, these disentangled chains can readily align along the applied stress direction, forming highly oriented extended-chain crystals that substantially enhance tensile strength and modulus [27–30].

Accurate characterization of chain entanglement in UHMWPE is crucial for material property optimization. Dynamic rheological analysis has emerged as the most reliable method, where time-sweep experiments monitoring the evolution of storage modulus (G') provide direct measurement of entanglement density through parameters such as the characteristic equilibration time for entanglement buildup (t_m) [31]. Differential scanning calorimetry (DSC) offers indirect assessment of entanglement state by analyzing melting-crystallization behavior, with disentangled samples typically exhibiting higher melting points (T_m) and crystallinity [32–36]. Small-angle *X*-ray scattering (SAXS) and wide-angle *X*-ray diffraction (WAXD) provide complementary information on the lamellar thickness and crystalline perfection, which are closely related to entanglement density [37–40]. Regarding entanglement control, low-temperature polymerization (typically 0–30 °C) serves as a key strategy, where enhanced crystallization kinetics limit chain interpenetration during growth [41]. Diluted catalyst concentrations increase inter-center spacing, minimizing interference between growing chains [23]. Furthermore, single-site homogeneous catalysts enable precise control over molecular weight distribution (MWD), avoiding additional entanglements caused by high MW fractions [42,43].

Compared to conventional heterogeneous Z-N catalysts, homogeneous catalyst-based polymerization systems offer distinct advantages for producing dis-UHMWPE.

Molecularly dispersed homogeneous catalysts such as metallocenes and bis(phenoxyimine) titanium (FI) complexes provide uniform active sites that precisely control the chain growth dynamics (**Figure 1**). This homogeneous catalytic environment ensures that all propagating chains experience similar microenvironments, substantially reducing entanglement formation due to spatial constraints. Importantly, the ligand architecture in these catalysts can be systematically modified to fine-tune activity and selectivity. For instance, incorporating sterically demanding ligands can retard propagation rates, creating favorable conditions for orderly chain arrangement. In contrast, heterogeneous catalysts suffer from carrier particles and multiple active sites that inevitably broaden molecular weight distributions and introduce irregular chain structures, thereby increasing entanglement probability. Additionally, the absence of supporting materials in homogeneous systems eliminates potential nucleation sites that might disrupt polymer crystallization, which is critical for obtaining highly regular, disentangled UHMWPE. These advantages collectively establish homogeneous catalyst-based polymerization the most promising route for producing high-performance dis-UHMWPE. This review systematically examines the transformative potential of dis-UHMWPE preparation based on homogeneous FI catalyst, with a focus on its intrinsic material properties, technological advantages, and methodologies for polymer preparation. The findings demonstrate that dis-UHMWPE is a pioneering material that simultaneously advances both sustainability and performance benchmarks in polyolefin materials science.

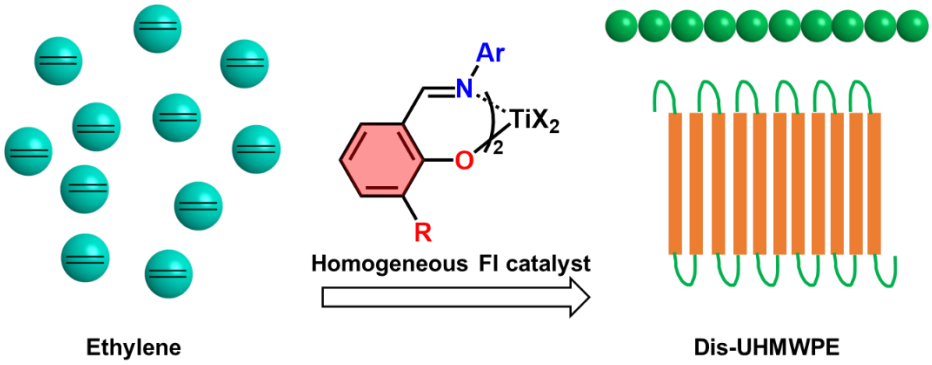

Figure 1. Schematic illustration for the preparation of dis-UHMWPE via homogeneous FI catalyst-based polymerization.

2. Outlines of homogeneous FI catalysts based polymerization

The development of dis-UHMWPE represents a paradigm shift in polyolefin technology, offering transformative solutions to the long-standing processing challenges associated with conventional UHMWPE while simultaneously enhancing its already exceptional mechanical performance. Among the various catalytic systems investigated for this purpose, bis(phenoxyimine) titanium complexes (commonly referred to as FI catalysts) have emerged as particularly promising due to their unique structural and catalytic characteristics [44]. This comprehensive discussion systematically examines the critical properties that render FI catalysts superior for dis-UHMWPE synthesis, provides a detailed comparison with traditional Z-N catalysts, and thoroughly explores the advantages of homogeneous catalyst-based

polymerization for the preparation of UHMWPE.

2.1. Essential properties of FI catalysts

FI Catalyst refers to a catalytic system whose main component is a Group IVB transition metal (Ti, Zr, or Hf) complex containing a bidentate phenoxy-imine (N, O-ligand) or analogous structural ligands [45] **(Figure 2)**. The quasi-living polymerization behavior demonstrated by FI catalysts under remarkably mild conditions (typically 0–30 °C and 1 atm ethylene pressure) represents one of their most significant advantages [46]. This characteristic enables unprecedented control over chain growth kinetics while effectively suppressing undesirable chain-transfer reactions such as *β*-hydride elimination, a prevalent issue in conventional Z-N catalysts that typically leads to broad MWD [47–49]. The living nature of FI-catalyzed polymerizations facilitates the synthesis of UHMWPE with exceptionally high MWs (routinely exceeding 3×10^6 g/mol) coupled with remarkably narrow molecular weight dispersity (*Đ*) typically ranging from 1.3 to 2.0 [50]. This precise control over polymer architecture is absolutely critical for achieving the low entanglement densities required for subsequent solid-state processing [42]. The living character of these polymerizations has been extensively studied through kinetic analyses, revealing propagation rate constants (k_p) on the order of 10^3–10^4 L/mol·s^{-1} at 25 °C, with activation energies of 30–50 kJ/mol that can be systematically tuned through strategic ligand modifications [51,52].

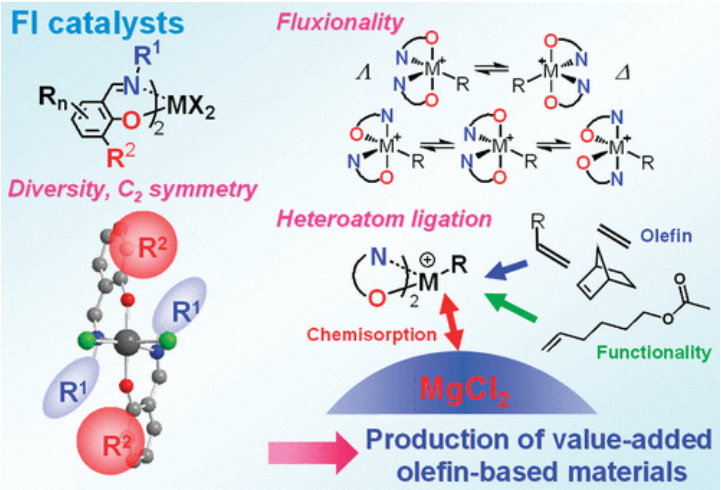

Figure 2. Schematic illustration of the structure and application of FI catalysts for olefin polymerization. Reprinted with permission from reference [45], copyright American Chemical Society 2009.

Unlike conventional heterogeneous Z-N catalysts that inherently possess multiple active sites with varying reactivity, FI catalysts operate through a perfectly homogeneous single-site mechanism [53]. This fundamental difference ensures that all active centers exhibit nearly identical kinetic behavior, completely eliminating the formation of low- and high-MW fractions that are characteristic of Z-N catalysts and contribute significantly to entanglement formation. This homogeneity results in polymers with perfectly uniform chain microstructure, which in turn facilitates controlled crystallization during polymerization and substantially reduces interchain

interactions [45,54]. The importance of this characteristic cannot be overstated, as it directly enables the production of UHMWPE reactor powders with the well-defined, low-entanglement structures required for advanced applications.

The modular ligand framework of FI catalysts provides unparalleled opportunities for systematic tuning of both steric and electronic properties [55]. For instance, the strategic introduction of tert-butyl (*t*-Bu) substituents at the ortho-position of the phenoxyimine ligand has been shown to simultaneously enhance thermal stability, increase propagation rates, and suppress undesirable chain-transfer reactions [56]. This tunability extends beyond simple steric effects. Electronic modifications through fluorinated aniline moieties can significantly alter the electrophilicity of the metal center, providing additional control over polymerization kinetics [55–57]. Such precise tuning capability enables optimization of the delicate balance between chain propagation and crystallization rates, which is absolutely crucial for favoring the formation of disentangled chain structures over entangled ones. Advanced computational studies, including DFT calculations, have provided valuable insights into the structure-activity relationships governing these effects, enabling rational catalyst design for specific applications [44].

2.2. Advantages of FI catalysts compared to Z-N catalyst

Traditional Z-N catalysts typically operate at elevated temperatures (60–100 ℃), conditions that inherently favor rapid chain propagation over crystallization [58–60]. This kinetic imbalance inevitably leads to the formation of highly entangled UHMWPE structures, with typical entanglement molecular weights (M_e) around 2000 g/mol [61]. Notably, the newly emerging ethylene polymerization via high-activity Z-N catalyst could also enable the production of UHMWPE under mild conditions, achieving efficient polymerization at 40–60 ℃ with low ethylene pressure [62–64]. In stark contrast, FI catalysts facilitate low-temperature polymerizations (commonly 10 ℃ or below), where crystallization kinetics can effectively compete with and often dominate over chain propagation [55]. This results in nascent powders with dramatically reduced entanglement densities, characterized by M_e values that frequently exceed 5000 g/mol [65]. The profound implications of this difference are also clearly evident in rheological studies, where FI-derived UHMWPE exhibits significantly longer t_m and lower plateau modulus (G_N^0) compared to Z-N catalyst products [42]. These rheological differences directly translate to vastly improved processability of the solid state.

The multi-site nature of Z-N catalysts inevitably produces UHMWPE with broad MW distributions ($Đ$ typically > 5), a direct consequence of the simultaneous operation of multiple active sites with differing reactivities [66]. This heterogeneity not only complicates processing but also introduces unpredictable variations in mechanical properties. FI catalysts, by virtue of their single-site character, consistently produce polymers with near-monodisperse chain lengths ($Đ$ < 2.0) [67]. This uniformity manifests in several critical advantages, including more predictable melt rheology, uniform stress distribution during solid-state deformation, and consistent mechanical properties in the final product [57] (**Figure 3**). Perhaps most importantly, the ability to achieve ultrahigh MWs (up to 9×10^6 g/mol) while maintaining narrow

distributions is unique to FI-type catalysts and is absolutely essential for producing high-performance dis-UHMWPE materials.

The superior architectural control afforded by FI catalysts enables solvent-free processing routes, marking a revolutionary advancement in UHMWPE technology [41]. Conventional Z-N catalyst-derived UHMWPE typically requires hazardous solvents (e.g., decalin) for dissolution during fiber spinning processes, presenting significant environmental and safety concerns [17]. In contrast, dis-UHMWPE produced via FI catalysts showed promising prospects in the field of solid-state processing techniques such as solid-state extrusion without solvent intervention [42,57]. This capability not only eliminates solvent handling issues but also dramatically reduces energy consumption by bypassing the solution concentration and solvent recovery steps in conventional processing. The economic and environmental benefits of this approach are substantial, potentially reducing production costs by up to 30% while simultaneously improving workplace safety.

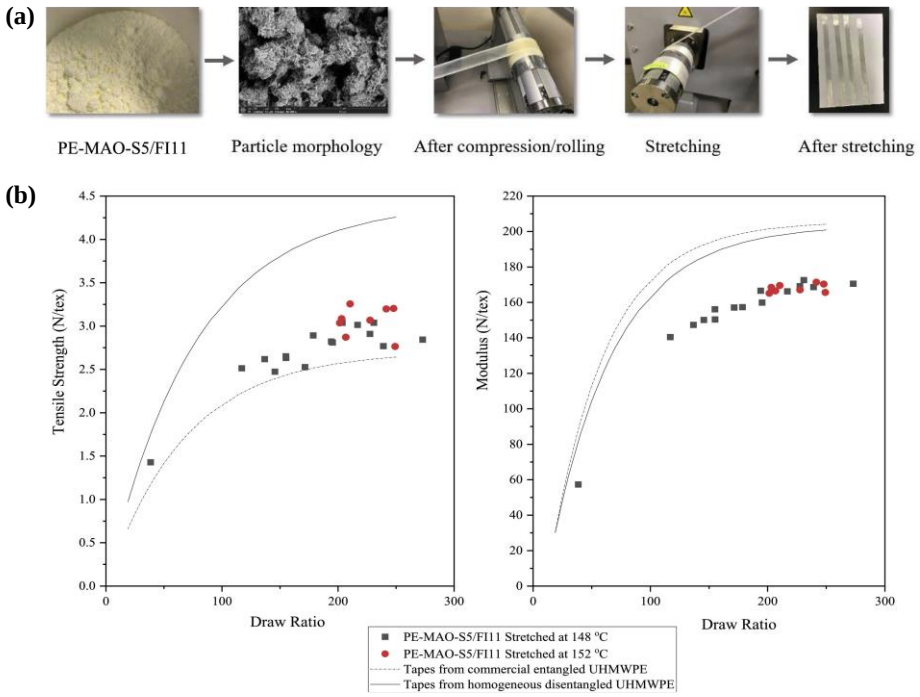

Figure 3. (a) The solid-state processing route for dis-UHMWPE; **(b)** the tensile strength and tensile modulus for dis-UHMWPE tapes made from homogeneous FI catalyst and commercial entangled UHMWPE tapes, respectively. Reprinted with permission from reference [57], copyright Elsevier 2024.

2.3. Advantages of polymerization based on homogeneous catalyst

Homogeneous catalyst-based polymerization has numerous remarkable technical advantages for the preparation of UHMWPE. In terms of the reaction system, its uniform nature eliminates mass and heat transfer non-uniformities that may occur in heterogeneous polymerization [68]. This enables more precise control of reaction conditions, effectively reduces side reactions, enables accurate MW control, and decreases the $Đ$, thus enhancing product quality stability. Regarding the polymerization reaction itself, homogeneous catalyst-based polymerization inhibits chain transfer and branching reactions (branching degree < 0.1 branches per 1000

carbon atoms), resulting in a linear molecular chain structure [41,69]. Combined with the low-temperature solution polymerization process (30–60 ℃), it can significantly reduce the chain entanglement density (50% lower than the traditional slurry method), enabling ultra-high draw ratios in dry spinning and breaking through the traditional trade-off between fiber strength and modulus [19]. From a perspective of polymer properties, it can produce UHMWPE with regular molecular chain structures and low chain entanglement degrees. The low-entanglement structure endows the polymer with good fluidity, greatly improving processability, reducing processing difficulty, and lowering energy consumption and costs during processing [43]. Moreover, this structure enhances the orientation and crystallization of molecular chains during the molding process, leading to higher strength and modulus in prepared fibers and other products, which presents clear advantages in high-end fields such as aerospace and national defense. Furthermore, homogeneous catalyst-based polymerization has high reaction activity and a fast polymerization rate, which can effectively improve production efficiency, reduce production costs per unit time in industrial production, enhance the economic benefits of enterprises, and strengthen the market competitiveness of products.

3. Recent progress of FI catalysts in dis-UHMWPE synthesis

Considering that UHMWPE is a material prized for its exceptional mechanical properties but hindered by its extreme melt viscosity due to chain entanglements, traditional melt-processing methods are impractical for UHMWPE (MW > 1×10^6 g/mol) because entanglement density escalates with MW, leading to prohibitive viscosity. Solvent-based routes, such as solution spinning, reduce entanglements but require large solvent volumes, complicating industrial scalability. Ronca et al. [70] aimed to address the inherent challenges in processing UHMWPE; they sought to develop a solvent-free synthesis route to produce dis-UHMWPE directly during polymerization, leveraging catalytic system modifications to suppress entanglements while maintaining processability and mechanical performance (**Figure 4**). They focused on optimizing a homogeneous, single-site catalytic system using an FI catalyst, i.e., bis[N-(3-tert-butylsalicylidene)pentafluoroanilinato]titanium (IV) dichloride ([3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$), paired with methylaluminoxane (MAO) as a cocatalyst. To mitigate the detrimental effects of trimethylaluminum (TMA) impurities in MAO, which deactivate catalytic sites and promote chain transfer, the cocatalyst was modified with 2,6-di-tert-butyl-4-methylphenol (BHT), which preferentially reacts with TMA to form inert complexes. Polymerizations were conducted under inert conditions (N_2/Ar) in toluene at 10 ℃ and 1.1 bar ethylene pressure for 60 min, varying BHT/MAO molar ratios (i.e., 0–0.6). Catalytic activity (R_p), assessed via ethylene uptake and normalized polymer yield, increased by up to 70% with BHT-modified MAO, attributed to reduced TMA interference. MW and MWD were estimated rheologically, with BHT-modified systems yielding higher MW (11×10^6 g/mol, MWD of 4.2) compared to standard MAO (MW of 9×10^6 g/mol, MWD of 3.4). Thermal analysis revealed consistent melting points (~139 ℃) and high crystallinity (77%–83%) across samples, while scanning electron microscopy (SEM) showed larger lamellar domains in dis-UHMWPE, indicative of reduced entanglement

density. Tensile tests demonstrated superior drawability at 125 ℃, with disentangled samples exhibiting gradual stress-elongation curves versus abrupt failure in commercial UHMWPE. Rheological time sweeps confirmed a metastable, low-entanglement melt state evolving into a fully entangled equilibrium, slower in BHT-modified systems due to higher MW. The study concluded that BHT-modified MAO enhances catalytic efficiency and MW while preserving reduced entanglement density critical for solid-state processing, making it a viable solvent-free pathway to high-performance UHMWPE with industrial applicability.

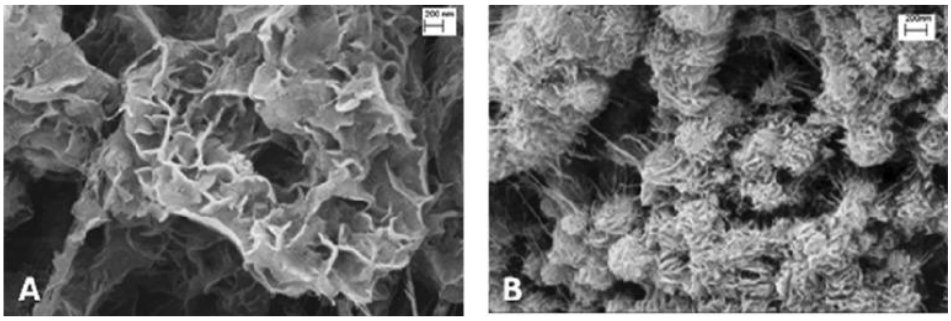

Figure 4. SEM images of: **(A)** PE2 (synthesized by a single-site catalyst); **(B)** commercial UHMWPE (synthesized by a heterogeneous, Z-N catalyst). The lamellae thickness is similar in both cases, but larger area lamellae are observed for PE2. Reprinted with permission from reference [70], copyright Wiley 2012.

Romano et al. [71] systematically investigated the synthesis of dis-UHMWPE using a homogeneous FI catalyst (i.e., [3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$/MAO/BHT) to address melt-processing challenges caused by high entanglement density. By varying ethylene pressure (1.1–4.1 atm) and reaction time (10–60 min) at 10 ℃, they produced dis-UHMWPE with weight-average MW of 2.3×10^6–34×10^6 g/mol and $Đ$ of 2.3–7.1. DSC analysis revealed a T_m of 139.4–140.3 ℃ and crystallinities of 75%–77%, while rheological studies showed that higher ethylene pressure increased both MW and entanglement density, evidenced by elevated G'. Slower melting kinetics observed during DSC annealing are correlated with increased inter-crystal entanglements at longer polymerization times and higher pressures. Mechanical testing demonstrated that tensile modulus increased with MW (up to 210 N/tex), whereas tensile strength peaked at MW of ~10×10^6 g/mol before declining due to entanglement-induced strain hardening, with higher-MW samples (> 10×10^6 g/mol) requiring greater drawing forces (> 1400 N/mm^2) but achieving lower ultimate strengths. The underlying reason could be that as the MW increases and the number of entanglement points grows, the deformation of the sample matrix becomes more difficult, thereby resulting in a higher modulus. Nevertheless, an increment in the number of entanglement points may give rise to the formation of relatively more stress-concentration points in the same sample. This seemingly poses an obstacle, like a stumbling block, to the transmission of external tension into the depths of the molecular chain. As a result, it is detrimental to the ability of the molecular chain's crystal structure to transmit and disperse forces, ultimately leading to a decrease in fracture strength. Overall, the study highlighted the critical role of polymerization kinetics in balancing entanglement reduction and MW optimization to produce high-

performance UHMWPE tapes for applications such as ballistic protection.

Based on the research mentioned above, Romano et al. [72] continue to explore the activation of a [3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$ catalyst with various aluminoxane co-catalysts to synthesize dis-UHMWPE, which exhibits superior processability and mechanical properties (**Figure 5**). The authors investigated MAO, polymethylaluminoxane (PMAO), and modified methylaluminoxane type 12 (MMAO12) and type 3A (MMAO3A), with BHT as a co-catalyst modifier to scavenge free trialkylaluminums. Polymerizations were conducted in toluene at 283 K under 1.1 bar ethylene pressure for 60 min. The FI/MAO-BHT system showed the highest activity (4.9×10^3 kg_{PE} mol_{cat}^{-1} h^{-1}), while MMAO3A-BHT increased activity tenfold compared to MMAO3A. Rheological analysis of the nascent polymer melt revealed low initial *G*' values (0.4–0.8 MPa), indicative of reduced entanglement density. DSC annealing experiments (411.3 K, 24 h) demonstrated that BHT-modified systems produced polymers with higher normalized melting areas, confirming lower entanglement. Uniaxial drawing of MMAO12-BHT-derived UHMWPE achieved tensile strengths of 4.3 N/tex (4.2 GPa) and a modulus of 220 N/tex (210 GPa), outperforming commercial entangled UHMWPE. The study concluded that co-catalyst choice and BHT addition critically influence catalyst activity, entanglement density, and mechanical properties, with MAO and MMAO12-BHT systems yielding optimal dis-UHMWPE. The findings underscored the role of co-catalyst structure in tuning polymer chain dynamics during synthesis.

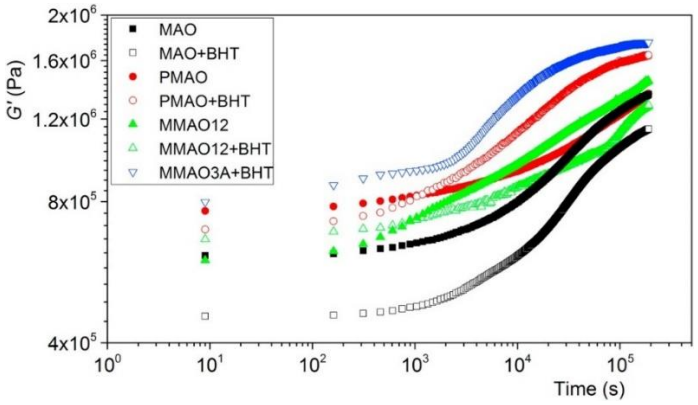

Figure 5. Elastic modulus buildup during polymer synthesis using different catalytic systems. The low values of *G*' indicate the low density of entanglements in the nascent polymer powder. Reprinted with permission from reference [72], copyright Elsevier 2015.

Previous studies by Smith and Lemstra demonstrated that reducing entanglement density through solution processing or controlled synthesis conditions could enhance processability, but the underlying mechanisms of entanglement formation during polymerization remained unclear [73–75]. To address this dilemma, Pandey et al. [76] aimed to investigate the heterogeneity in the distribution of entanglement density during the polymerization of dis-UHMWPE using a homogeneous single-site catalytic system, specifically addressing the influence of polymerization time and temperature on the resultant entangled state and molecular characteristics (**Figure 6**). The authors employed a homogeneous bis(phenoxyimine)titanium dichloride catalyst ([3-*t*-Bu-2-

O-$C_6H_3CH=N(C_6F_5)]_2TiCl_2$) activated by MAO in toluene under atmospheric ethylene pressure, ensuring a living polymerization system with a narrow MWD. By conducting polymerization at low temperatures (10–70 °C) and short times (1–30 min) under atmospheric ethylene pressure, they achieved dis-UHMWPE (MW of 0.3–6.3 × 10^6 g/mol) with narrow MWDs (i.e., 1.4–3.1), as determined by dynamic rheology, which is a technique validated for UHMWPE characterization where traditional GPC methods fall short. The catalyst exhibited high activity (10,330 kg_{PE} mol_{cat}^{-1} h^{-1} at 10 °C for 1 min), though activity declined with prolonged time and elevated temperatures due to reduced ethylene solubility and potential deactivation. Rheological analysis revealed heterogeneous entanglement formation, with higher entanglement density during initial polymerization stages, when local temperatures and catalyst activity peaked, followed by a decline as crystallization dominated over polymerization kinetics. The findings were corroborated by dynamic time sweep experiments, which showed that the time required for entanglement buildup in the melt state scaled with MW to a power of ~2.6, lower than the ~3.0 expected for reptation dynamics in a thermodynamically stable melt, suggesting faster entanglement formation in the initially disentangled state. The study demonstrated that controlled polymerization conditions, particularly low temperatures and homogeneous catalysis, can enable the synthesis of dis-UHMWPE by balancing polymerization and crystallization kinetics, offering a pathway to overcome processing challenges while maintaining superior mechanical properties for advanced applications.

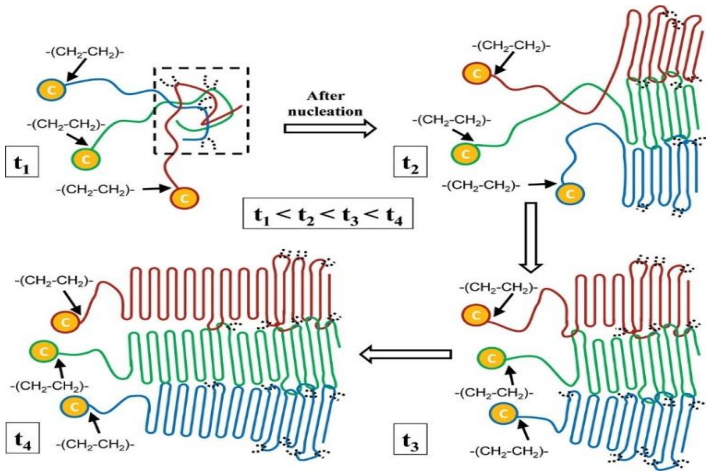

Figure 6. Schematic illustration of chain growth and entanglement evolution during polymerization and crystallization. The diagram depicts chain growth from three catalytic sites, where entanglements (dotted black loops) form between neighboring chains (red, blue, green) in the early stages before crystallization. A discontinuous rectangular box highlights entanglement formation prior to crystallization, leading to an entangled crystalline state at t_2. Upon nucleus formation away from the exothermic catalytic site, the nucleation barrier is suppressed, accelerating crystal growth (t_3). As polymer crystals form around the catalyst, ethylene diffusion decreases, slowing polymerization. This kinetic reduction, combined with lowered nucleation barriers, promotes crystallization of growing chains, ultimately yielding high MW dis-polyethylene (t_4). Reprinted with permission from reference [76], copyright American Chemical Society 2011.

Forte et al. [77] systematically studied the synthesis of dis-UHMWPE using a homogeneous [3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$ catalyst activated by MAO in different solvent systems, focusing on the unexpected synergistic effects in toluene/heptane mixtures. The research aimed to address two challenges in UHMWPE technology, i.e., high melt viscosity due to chain entanglements and the need for solvent-free processing routes. They used a well-defined homogeneous catalytic system under mild conditions (10 °C, 1.1–1.4 bar ethylene pressure, Al/Ti ratio of 1200) based on previous work. Through experiments in 1 L and 10 L reactors, they explored the impacts of catalyst concentration (2.5–40 μM) and solvent composition on catalytic activity, molecular characteristics, and polymer morphology. The results showed that catalytic activity peaked at 15 μM in toluene. Solvent mixtures had non-linear effects on activity, with a 70/30 toluene/heptane mixture showing the highest activity (2500 $kg_{PE}\ mol_{cat}^{-1}\ h^{-1}$ in a 1 L reactor, 2900 $kg_{PE}\ mol_{cat}^{-1}\ h^{-1}$ in a 10 L reactor). This was due to toluene's promotion of catalyst/MAO ionic dissociation and heptane's high ethylene solubility. The produced polymers had MWs of 0.9–2.3×10^6 g/mol (number-average molecular weight, M_n) and 3.0–7.6×10^6 g/mol (weight-average molecular weight, M_w), with $Đ$ of 2.0–4.3, and the 50/50 toluene/heptane mixture gave the narrowest $Đ$ (i.e., 2.0). SEM analysis revealed striking morphological differences, i.e., pure toluene yielded large and loosely stacked lamellae, while heptane produced smaller and densely packed aggregates, with intermediate morphologies in mixed solvents. The study concluded that the optimal 70/30 toluene/heptane composition maximized catalytic activity and improved polymer morphology while maintaining the disentangled state. The synergistic effect was attributed to balanced monomer availability and catalyst activation kinetics. These findings deepen the understanding of solvent effects in homogeneous catalytic olefin polymerization and offer practical guidance for dis-UHMWPE production scale-up, though further research on catalyst-solvent interface interactions using advanced spectroscopic techniques is needed.

Rastogi et al. [78] investigated the synthesis and solvent-free solid-state processing of dis-UHMWPE using a homogeneous [3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$ catalyst activated by MAO (**Figure 7**). The goal of the research aimed to bypass the solvent-intensive gel-spinning method, which requires dissolving UHMWPE in high-boiling-point solvents, by directly synthesizing low-entanglement polymers through controlled polymerization. The FI catalyst, operating under low temperature and concentration conditions (10 °C, 1 bar ethylene pressure, 8.3 μM catalyst in toluene), produced dis-UHMWPE with MW of ~2.8 × 10^6 g/mol and $Đ$ of 3.0. The polymerization mechanism ensured spatial separation of active sites and rapid chain crystallization, yielding loosely packed lamellar crystals with 20 nm thickness, as confirmed by SEM. The solid-state nuclear magnetic resonance (NMR) spectra revealed faster segmental exchange between amorphous and crystalline regions in dis-UHMWPE compared to entangled UHMWPE (e-UHMWPE), indicating reduced topological constraints. The solvent-free processing involved compression molding at 129 °C followed by sequential uniaxial or biaxial stretching at 125–145 °C, achieving draw ratios exceeding 180. The resultant tapes exhibited exceptional mechanical properties, including tensile strength up to 3.8 N/tex (3.7 GPa) and modulus up to 200 N/tex (196 GPa), surpassing solution-spun fibers (e.g., Dyneema SK75, modulus 135 GPa). *X*-ray diffraction (XRD) and NMR analysis

showed enhanced performance with high crystallinity (95%) and a preferential orthorhombic crystal plane orientation (CPO > 7), which amplified van der Waals interactions between aligned chains. In contrast, e-UHMWPE processed under similar conditions showed lower crystallinity (84%) and strength (2.3 N/tex) due to residual entanglements and partial melting during deformation. The study also demonstrated the unprecedented biaxial stretching of dis-UHMWPE into isotropic films (8 μm thickness, 0.7 GPa strength), highlighting its versatility for advanced applications. The findings underscored the critical role of entanglement control in optimizing solid-state processability and mechanical performance, positioning dis-UHMWPE a viable alternative to solvent-dependent manufacturing routes.

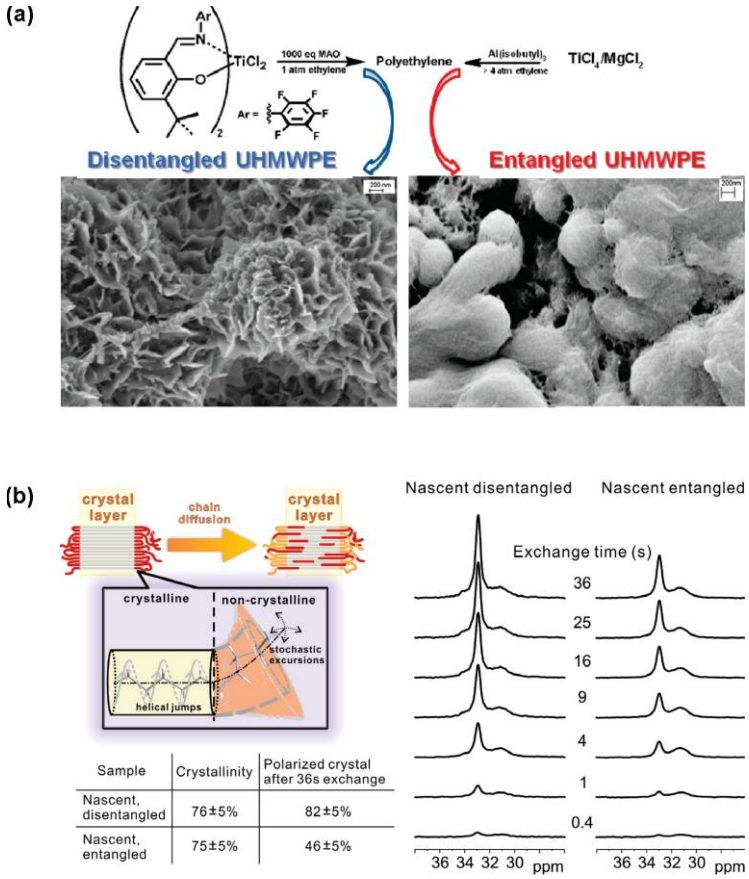

Figure 7. The morphological and molecular distinction in the nascent UHMWPE polymers: **(a)** A comparison of SEMs obtained on UHMWPE samples synthesized using homogeneous (left) and heterogeneous (right) catalysts; **(b)** Morphological differences depicted in **(a)** can be observed at the segmental level by following the diffusion of linear polyethylene methylene from amorphous to crystalline regions. Reprinted with permission from reference [78], copyright American Chemical Society 2011.

Talebi et al. [79] investigated the characterization challenges of UHMWPE with M_w exceeding 1×10^6 g/mol, where conventional gel permeation chromatography (GPC) becomes unreliable due to high viscosities and incomplete mass recovery (below 90% for $M_w > 5 \times 10^6$ g/mol). The study employed a living homogeneous catalytic system consisting of [3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$ activated by

MAO at Al/Ti ratios of 5000–15,000, which enabled precise control over polymerization under inert conditions (toluene, 20 ℃, 1 bar ethylene pressure). Polymerization conducted at −15 to 30 ℃ for 1–30 min produced UHMWPE with controlled MWs (M_w, 2.0–9.1 × 10^6 g/mol, M_n, > 1 × 10^6 g/mol) and narrow $Đ$ (1.3–2.6), where shorter reaction times yielded the narrowest $Đ$ (1.3). These results demonstrated the profound impact of polymerization time and temperature on the molecular properties of UHMWPE. Such findings are of great significance for optimizing the polymerization process and custom-tailoring UHMWPE to meet the requirements of diverse applications. Moreover, solid-state NMR confirmed the linear, unbranched architecture of the synthesized polymers. Notably, the researchers developed an advanced rheological methodology based on the modulus model and stress-relaxation experiments, incorporating double reptation theory (β = 2) with a single exponential kernel function to convert relaxation spectra into MWD curves. This approach extended the measurable frequency range to 10^{-7} rad/s through time-molar mass superposition, demonstrating superior accuracy compared to GPC, particularly for samples with MW higher than 5 × 10^6 g/mol, where GPC showed significant discrepancies. Therefore, the study established melt rheometry as a robust alternative for characterizing ultra-high-molar-mass polymers while simultaneously validating the living homogeneous catalyst system's capability to produce dis-UHMWPE with precisely controlled molecular architectures. These findings have significant implications for advanced materials applications that require tailored polymer properties, such as high-performance fibers, where precise control over molar mass and entanglement density is crucial. The work highlighted the importance of selecting appropriate characterization techniques based on polymer properties and demonstrated the potential of living polymerization systems for synthesizing polyolefins with precisely engineered structures.

Li et al. [80] studied the impact of polyhedral oligomeric silsesquioxane (POSS) structure on the disentangled state of UHMWPE nanocomposites prepared via in situ ethylene polymerization (**Figure 8**). Given the challenge of reconciling UHMWPE's excellent mechanical properties with its poor processability from excessive chain entanglements, this research aimed to develop dis-UHMWPE for applications like high-performance fibers and films. A homogeneous single-site catalytic system with the [3-*t*-Bu-2-O-C_6H_3CH=N(C_6F_5)]$_2TiCl_2$ activated by MAO physically adsorbed onto three alkyl-POSS variants was used. Polymerization in toluene at 30 ℃ under 1 bar ethylene pressure with an [Al]/[Ti] molar ratio of 16,000 yielded UHMWPE with ultrahigh MWs (i.e., 1.04–2.20 × 10^6 g/mol) and narrow MWD (2.1–3.6). The FI catalyst retained its living polymerization features but had reduced activity in the presence of alkyl-POSS, with activity decreasing in the order FI catalyst > FI/methyl-POSS > FI/cyclohexyl-POSS > FI/phenyl-POSS due to POSS substituents' electron-donating effects. The nanocomposites showed enhanced crystallinity (i.e., 44.8%–48.6%) and a lamellar thickness, with methyl- and cyclohexyl-POSS acting as nucleating agents. Transmission electron microscopy (TEM) showed a uniform dispersion of methyl- and cyclohexyl-POSS, while phenyl-POSS aggregated. Rheological analysis indicated that the nascent UHMWPE/POSS nanocomposites were initially disentangled but formed entanglements faster than pure UHMWPE during melt-state annealing. The entanglement buildup time was inversely

proportional to the strength of POSS-polymer interactions, with cyclohexyl-POSS providing the most disentangled structure due to steric hindrance. Phenyl-POSS produced higher-MW polymers with slower entanglement formation. The study concluded that alkyl-POSS incorporation modulates UHMWPE's disentangled state through nucleating effects and physical adsorption, with cyclohexyl-POSS offering the optimal balance. These results show the potential of tailored POSS catalysts for engineering dis-UHMWPE, though there are challenges in uniform POSS dispersion and polymerization kinetics control. Future research could explore hybrid catalytic systems or advanced characterization techniques to better understand entanglement formation dynamics during in-situ polymerization.

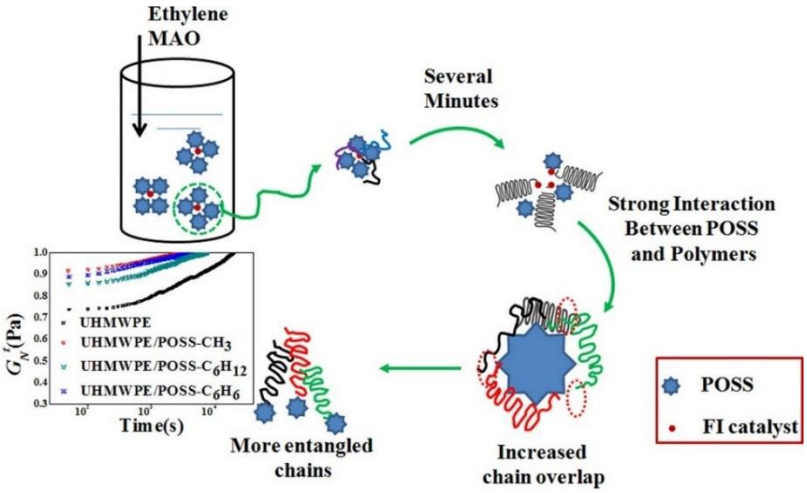

Figure 8. Proposed procedure for the formation of disentangled structures in the nascent UHMWPE matrix. Reprinted with permission from reference [80], copyright American Chemical Society 2015.

Besides, Li et al. [81] also investigated the synthesis of dis-UHMWPE/POSS nanocomposites via ethylene in situ polymerization, with the aim of uncovering the impact of POSS nanoparticles on entanglement dynamics and crystallization behavior. The study is driven by the need to enhance the thermal and mechanical properties of dis-UHMWPE while maintaining its processability. A homogeneous catalytic system was employed, where the FI catalyst, [3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$, was immobilized on disilanolisobutyl POSS through hydroxyl-Ti interactions. Methyl-POSS and FI/cyclohexyl-POSS can achieve a homogeneous state in toluene. The homogeneous state can still be maintained when the POSS reacts with the FI catalyst. Polymerization was conducted at 30 °C in toluene with MAO as a cocatalyst ([Al]/[Ti] = 16,000), yielding UHMWPE/POSS nanocomposites with POSS loadings of 0.7–2.3 wt%. The FI/POSS system showed reduced catalytic activity (0.68–0.88 × 10^3 kg_{PE} mol_{cat}^{-1} h^{-1}) compared to pure FI catalyst (1.59 × 10^3 kg_{PE} mol_{cat}^{-1} h^{-1}), which was attributed to restricted chain propagation near POSS surfaces. The resulting polymers exhibited high MWs (1.28–3.47 × 10^6 $g \cdot mol^{-1}$) and a broad MWD (2.73–4.95). Rheological analysis revealed increased entanglement density in the nanocomposites, evidenced by shorter modulus buildup times and higher plateau modulus. DSC showed enhanced crystallinity (66%–75%) and lamellar thickness due to POSS acting as a

nucleating agent, with T_m rising from 134.6 °C (pristine dis-UHMWPE) to 136.4–143.6 °C. The study concluded that POSS incorporation improves thermal stability (decomposition onset > 370 °C) and hydrophilicity (contact angle reduction from 98° to 85°) but compromises the disentangled state, underscoring the trade-off between functionalization and entanglement control.

Motivated by the challenges associated with processing conventional UHMWPE due to its high melt viscosity and entangled chain structure, Chen et al. [82] aimed to investigate the phase structure and mechanical properties of dis-UHMWPE nanocomposites incorporating polyhedral oligomeric silsesquioxane (POSS). They sought to develop nanocomposites with improved mechanical performance and processability by leveraging the unique properties of POSS nanoparticles, which can act as nucleating agents and enhance polymer crystallinity while reducing chain entanglements. The authors employed an in situ ethylene polymerization approach using a homogeneous catalytic system consisting of a [3-*t*-Bu-2-O-$C_6H_3CH{=}N(C_6F_5)]_2TiCl_2$ catalyst activated by MAO in toluene at 30 °C under 1 bar ethylene pressure. This method ensured uniform dispersion of POSS nanoparticles within the UHMWPE matrix, as confirmed by TEM. The resulting nanocomposites exhibited MW ranging from 1.28×10^6 to 2.33×10^6 g/mol and MWDs from 2.19 to 4.33, depending on the POSS loading (0–2.3 wt%). Wide-line proton NMR and ^{13}C CP/MAS solid-state NMR revealed that POSS incorporation significantly increased crystallinity (up to 68.58%) and hindered chain mobility in the intermediate and monoclinic phases, while enhancing mobility in the amorphous phase due to reduced entanglements. Mechanical testing demonstrated that a 1 wt% POSS loading optimized tensile strength (65 MPa) and reduced friction coefficients, attributed to the uniform dispersion of POSS and its role as a molecular-scale lubricant. Rheological studies indicated improved melt recovery properties, suggesting that POSS-polymer interactions formed a mechanical network enhancing flow stability. The study concluded that dis-UHMWPE/POSS nanocomposites, synthesized via in situ polymerization, exhibit superior crystallinity, mechanical properties, and processability, with POSS acting as a nucleating agent and entanglement reducer. These findings highlighted the potential of POSS-based nanocomposites for advanced applications requiring high-performance UHMWPE while also providing insights into the relationship between nanofiller dispersion, phase structure, and macroscopic properties. Future research could examine the scalability of this method and the long-term stability of POSS-UHMWPE interactions under operational conditions.

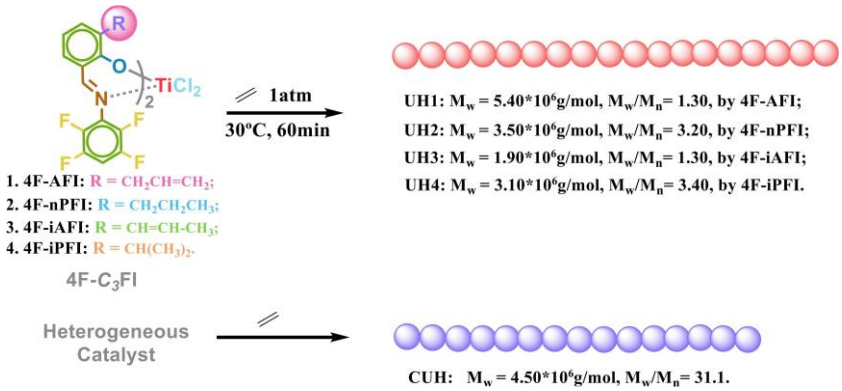

Figure 9. Schematic illustration for the dis-UHMWPE (UH1–UH4) synthesized by tetra-fluorinated FI catalysts. Reprinted with permission from reference [83], copyright Elsevier 2024.

Notably, the substituents on the benzene ring of the FI catalyst can be fine-tuned for the polymerization of dis-UHMWPE. Wang et al. [83] elucidated the role of catalyst architecture, specifically the electronic and steric effects of C_3 substituents in fluorinated phenoxy-imine (FI) catalysts, on the non-isothermal crystallization kinetics of nascent dis-UHMWPE (**Figure 9**). The research was motivated by the need to optimize melt-processing performance, as dis-UHMWPE crystallization behavior critically influences its solidification dynamics during industrial shaping processes. Four FI catalysts with varying C_3 substituents (allyl(A), *n*-propyl(nP), 1-propenyl(i), isopropyl(ip)) were employed under homogeneous catalytic ethylene polymerization conditions (1 atm, 30 °C, 60 min) to synthesize dis-UHMWPEs (UH1–UH4). Catalyst activity followed the order 4F-AFI > 4F-nPFI ≈ 4F-iPFI > 4F-iAFI, yielding UHMWPEs with MW ranging from 1.9 × 10^6 to 5.4 × 10^6 g/mol and narrow dispersities ($Đ$ = 1.3–3.4). All polymers exhibited high linearity, as illustrated by ^{13}C NMR and crystallinities (73.8%–80.8%). Rheological analysis revealed lower initial elastic moduli (0.08–0.31 MPa at 170 °C) compared to commercial UHMWPE (0.31 MPa), confirming reduced entanglement densities. Non-isothermal crystallization studies using DSC and isoconversional kinetic analysis demonstrated that crystallization rates at low supercooling (cooling rates ≤ 10 K/min) inversely correlated with the molar fraction of nascent entangled crystals, which was governed by the substituent's electron-donating capacity and steric bulk. For instance, UH3 (from 4F-iAFI with a 1-propenyl group) exhibited the fastest crystallization due to minimal entanglement, while UH4 (from 4F-iPFI with an isopropyl group) showed slower kinetics due to steric hindrance that promotes entanglement. At high supercooling (> 10 K/min), crystallization kinetics became independent of the catalyst architecture, dominated instead by nucleation-driven chain reorganization. The study concluded that precise control over substituent electronic and steric properties in FI catalysts enables tuning of the dis-UHMWPE entanglement state and crystallization behavior, providing critical insights for designing melt-processable UHMWPEs with tailored solidification dynamics.

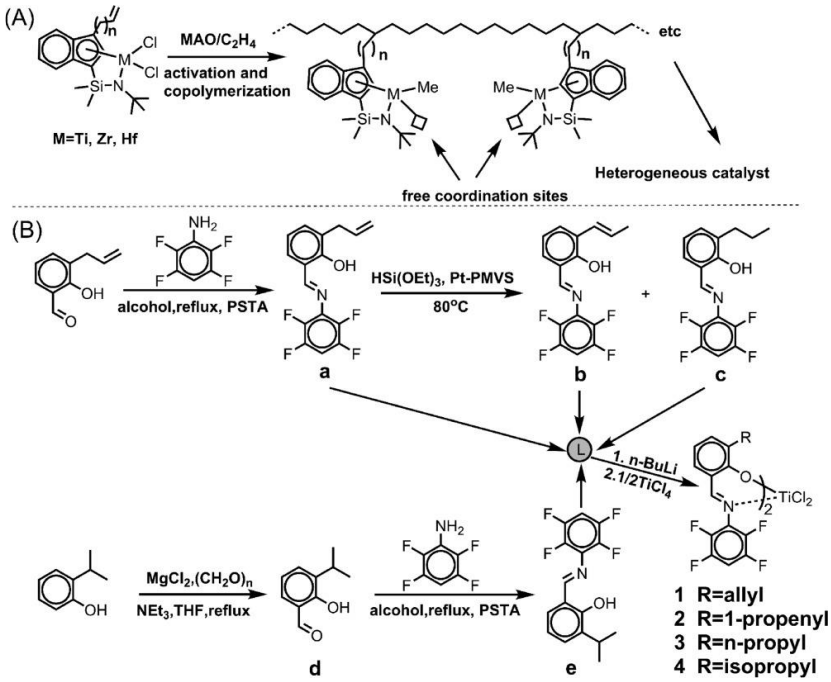

Figure 10. (A) The classic self-immobilization mechanism of the *ω*-alkenyl substituted constrained geometry catalysts (CGCs); **(B)** synthesis route of complexes 1–4. Reprinted with permission from reference [84], copyright Wiley 2016.

Besides, Wang et al. [84] further used a homogeneous catalyst-based polymerization system with a series of alkenyl- and alkyl-substituted phenoxy-imine titanium catalysts (complexes 1–4) activated by MAO in ethylene polymerization (**Figure 10**). Polymerizations were carried out in toluene under mild conditions (atmospheric ethylene pressure, 10–50 °C, 15–60 min) with an Al/Ti ratio of 2000. The allyl-substituted complex 1 had the highest activity (2.2–3.4 $kg_{PE}\cdot mmol_{cat}^{-1}\cdot h^{-1}$) and produced UHMWPE with the highest M_W up to 5.4×10^6 $g\cdot mol^{-1}$ and narrow $Đ$ of 1.3–1.9), while the 1-propenyl-substituted complex 2 had the lowest activity (0.25–0.71 $kg_{PE}\cdot mmol_{cat}^{-1}\cdot h^{-1}$) and produced the lower-MW dis-UHMWPE (M_w = 0.66–1.9 $\times 10^6$ $g\cdot mol^{-1}$, $Đ$ = 1.3–2.4). All catalysts generated UHMWPE with high crystallinity (72.2%–82.3%) and T_m (137.9–141.2 °C). Furthermore, ^{13}C NMR analysis showed different levels of short-chain branching, with complex 1 introducing three types of short-chain branching species (methyl: 0.32; isobutyl: 1.15; 2-methylhexyl: 0.39 branches/1000C), complex 2 having more branches (2.68 branches/1000C), and complexes 3 and 4 having fewer branches (0.97 and 0 branches/1000C, respectively). In conclusion, alkenyl substituents, especially terminal allyl groups, can enhance catalytic activity and introduce controlled SCBs through a proposed "self-immobilization" mechanism. The allyl-substituted catalyst 1 offered a good balance among high MW, narrow $Đ$, and moderate branching, which is promising for dis-UHMWPE synthesis. However, the unexpected formation of isobutyl and 2-methylhexyl branches indicated a unique mechanism that needs further study. Overall, this research proposed ideas for the structural design of FI catalysts, which helps to improve the processing and mechanical properties of UHMWPE.

4. Future perspectives

During the industrial production of dis-UHMWPE using FI catalysts, several core challenges need to be addressed. Firstly, the high cost and stability issues with the MAO co-catalyst are urgent problems. Current research is focused on developing alternative activation systems, designing supported FI catalysts to reduce the amount of MAO used, and optimizing the MAO synthesis process. Secondly, the scale-up of low-temperature polymerization (≤ 30 ℃) requires breaking through engineering bottlenecks, including the development of multi-zone circulation reactors integrated with cooling systems, the use of high-boiling solvent mixtures (such as heptane/toluene), and advanced temperature control technologies. Thirdly, the transition from laboratory batch processes to continuous production requires the reconstruction of the reactor design. Key points include adapting to loop slurry/gas-phase processes, developing precise feed systems, and exploring FI/Z-N catalyst systems. The feasibility of these innovations has been verified through pilot tests, but energy efficiency optimization remains crucial. Furthermore, it is worth mentioning that during the process of catalytic ethylene polymerization to produce UHMWPE, the product is usually dispersed in solid particles in hydrocarbon solvents (such as hexane and heptane), and achieving efficient separation is crucial for industrialization. Currently, centrifugal filtration or depressurization solvent removal technology is widely used, but it faces the problems of decreased purity and high energy consumption caused by fine powder carrying solvents. Future research may focus on developing novel solvent systems (such as supercritical CO_2-assisted separation) or surface-modified catalyst supports to regulate polymer morphology and reduce solvent adsorption. Additionally, using high-temperature flash evaporation or adding anti-static agents can significantly improve powder flowability and enhance separation efficiency, which is of great significance for continuous production processes.

To make large-scale application of FI catalysts, a trinity technical approach is necessary. At the catalyst level, new activation systems independent of MAO or stabilized supported catalysts are worth developing. At the process level, modular low-temperature continuous polymerization systems could be designed, combined with supercritical fluid technology to enhance heat transfer. At the production level, intelligent control systems could be developed to regulate molecular weight and distribution in real-time and to establish compatibility solutions with existing polyolefin plants. Particularly noteworthy is the hybrid catalyst technology. Combining Z-N catalysts with FI catalysts to prepare UHMWPE or UHMWPE with narrow MWD through synergistic polymerization may be a challenging but scientifically significant research direction.

Once the industrial bottlenecks are overcome, FI-catalyzed dis-UHMWPE will reshape the landscape of the high-performance polyolefin industry. In the medical field, its excellent biocompatibility and processability will drive the upgrading of implantable devices such as artificial joints. In the field of protective materials, the ultra-high-strength fibers ($\sigma > 3$ GPa) prepared by solid-state processing are expected to replace aramid fibers in bulletproof equipment. In the new energy field, its high modulus property is ideal for reinforcing materials in lithium battery separators. A more far-reaching impact is the establishment of a new green manufacturing paradigm,

i.e., the solvent-free process can reduce the use of organic solvents, and combined with the low-carbon characteristics of low-temperature polymerization, the carbon footprint throughout the life cycle can be significantly reduced.

5. Conclusions

The synthesis of dis-UHMWPE through homogeneous catalyst-based polymerization, particularly using FI catalysts, represents a significant advancement in polyolefin technology. FI catalysts exhibit unparalleled control over polymer architecture, leveraging their living polymerization behavior, single-site homogeneity, and tunable steric/electronic effects to produce UHMWPE with ultrahigh MWs, narrow polydispersity, and significantly reduced entanglement densities. These characteristics demonstrate promising prospects in solvent-free solid-state processing, overcoming the long-standing challenges of conventional UHMWPE, such as prohibitive melt viscosity and poor processability. Comparative studies highlight the superiority of FI catalysts over traditional Z-N catalysts, with FI-derived dis-UHMWPE demonstrating enhanced mechanical properties and thermal stability. Moreover, key innovations include the optimization of cocatalysts (e.g., MAO modified with BHT), low-temperature polymerization, and precise control over reaction kinetics to balance chain propagation and crystallization. Despite these advancements, industrial scalability remains a challenge, necessitating innovations in catalyst stabilization, reactor design, and continuous production processes. The future direction should focus on developing optimized catalysts, polymerization conditions, and advanced characterization techniques to fully unlock the potential of dis-UHMWPE for high-performance applications in the medical, ballistic, and energy sectors. In conclusion, FI-catalyzed dis-UHMWPE not only redefines the boundaries of polyolefin performance but also sets new benchmarks for sustainable polymer processing.

Conflict of interest: The author declares no conflict of interest.

References

1. Hussain M, Naqvi RA, Abbas N, et al. Ultra-High-Molecular-Weight-Polyethylene (UHMWPE) as a Promising Polymer Material for Biomedical Applications: A Concise Review. Polymers. 2020; 12(2): 323. doi: 10.3390/polym12020323
2. Kamal A, Bashir M, Firdous S, et al. Optical properties of ultra-high molecular weight polyethylene (UHMWPE): A material of choice for total joint applications. Radiation Physics and Chemistry. 2016; 118: 102-106. doi: 10.1016/j.radphyschem.2015.03.012
3. Eun JH, Kim DH, Jang IU, et al. A study on mechanical properties and thermal properties of UHMWPE/MWCNT composite fiber with MWCNT content and draw ratio. Journal of Engineered Fibers and Fabrics. 2022; 17. doi: 10.1177/15589250221108484
4. Joshi A, Mishra A, Saxena VK. Impact response and energy absorption mechanisms of UHMWPE fabric and composites in ballistic applications: A comprehensive review. Composites Part A: Applied Science and Manufacturing. 2024; 185: 108314. doi: 10.1016/j.compositesa.2024.108314
5. Forster AL, Forster AM, Chin JW, et al. Long-term stability of UHMWPE fibers. Polymer Degradation and Stability. 2015; 114: 45-51. doi: 10.1016/j.polymdegradstab.2015.01.028
6. Huang J, Zhang X, Gu T, et al. Effect of Hot-Pressing Process on Mechanical Properties of UHMWPE Fiber Non-Woven Fabrics. Materials. 2024; 17(11): 2611. doi: 10.3390/ma17112611

7. Panin SV, Kornienko LA, Alexenko VO, et al. Increasing Wear Resistance of UHMWPE by Loading Enforcing Carbon Fibers: Effect of Irreversible and Elastic Deformation, Friction Heating, and Filler Size. Materials. 2020; 13(2): 338. doi: 10.3390/ma13020338
8. Mohammed AS, Fareed MI. Improving the friction and wear of poly-ether-etherketone (PEEK) by using thin nano-composite coatings. Wear. 2016; 364-365: 154-162. doi: 10.1016/j.wear.2016.07.012
9. Faruk O, Yang Y, Zhang J, et al. A Comprehensive Review of Ultrahigh Molecular Weight Polyethylene Fibers for Applications Based on Their Different Preparation Techniques. Advances in Polymer Technology; 2023. doi: 10.1155/2023/6656692
10. Quero A, Colli M, Silvestro I, et al. UHMWPE composites: Effect of flame retardant tannic acid as coating agent and hardener for epoxy resin systems. Polymer Composites; 2025. doi: 10.1002/pc.30020
11. Wahed S, Dunstan C, Boughton P, et al. Functional Ultra-High Molecular Weight Polyethylene Composites for Ligament Reconstructions and Their Targeted Applications in the Restoration of the Anterior Cruciate Ligament. Polymers. 2022; 14(11): 2189. doi: 10.3390/polym14112189
12. Wang J, Guo Y, Su Y, et al. New Trends in Ballistic UHMWPE UD Fabric. Journal of Physics: Conference Series. 2023; 2460(1): 012105. doi: 10.1088/1742-6596/2460/1/012105
13. Wu S, Sikdar P, Bhat GS. Recent progress in developing ballistic and anti-impact materials: Nanotechnology and main approaches. Defence Technology. 2023; 21: 33-61. doi: 10.1016/j.dt.2022.06.007
14. He J, Wang Y, Qian Y, et al. Surface Modification of Ultra-High-Molecular-Weight Polyethylene and Applications: A Review. Polymers. 2024; 16(23): 3431. doi: 10.3390/polym16233431
15. Shelly D, Lee SY, Park SJ. Compatibilization of ultra-high molecular weight polyethylene (UHMWPE) fibers and their composites for superior mechanical performance: A concise review. Composites Part B: Engineering. 2024; 275: 111294. doi: 10.1016/j.compositesb.2024.111294
16. Li L, Duan Y. Engineering Polymer-Based Porous Membrane for Sustainable Lithium-Ion Battery Separators. Polymers. 2023; 15(18): 3690. doi: 10.3390/polym15183690
17. Li L, Kong F, Xiao A, et al. Current research status of high-performance UHMWPE fiber: A review. Materials Technology Reports. 2024; 2(2): 1518. doi: 10.59400/mtr1518
18. Dong P, Wang K, Li JF, et al. Chain entanglement regulation of sintered ultrahigh molecular weight polyethylene and its effect on properties. Acta Polymerica Sinica. 2020; 51(1): 117-124. doi: 10.11777/j.issn1000-3304.2020.19159
19. Rastogi S, Lippits DR, Peters GWM, et al. Heterogeneity in polymer melts from melting of polymer crystals. Nature Materials. 2005; 4(8): 635-641. doi: 10.1038/nmat1437
20. Li W, Hui L, Xue B, et al. Facile high-temperature synthesis of weakly entangled polyethylene using a highly activated Ziegler-Natta catalyst. Journal of Catalysis. 2018; 360: 145-151. doi: 10.1016/j.jcat.2018.01.024
21. Wang H, Yan X, Tang X, et al. Contribution of the Initially Entangled State and Particle Size to the Sintering Kinetics of UHMWPE. Macromolecules. 2022; 55(4): 1310-1320. doi: 10.1021/acs.macromol.1c02058
22. Li L, Pan W, Kong F, et al. Engineering polyvinylidene fluoride–based lithium-ion battery separators via blending modification. Academia Engineering. 2025; 2(1). doi: 10.20935/acadeng7608
23. Li L, Kong F, Xiao A, et al. Preparation of nascent disentangled ultra-high molecular weight polyethylene based on Ziegler-Natta catalyst. Materials Technology Reports. 2025; 3(1): 2305. doi: 10.59400/mtr2305
24. Chammingkwan P, Bando Y, Mai LTT, et al. Less Entangled Ultrahigh-Molecular-Weight Polyethylene Produced by Nano-Dispersed Ziegler–Natta Catalyst. Industrial & Engineering Chemistry Research. 2021; 60(7): 2818-2827. doi: 10.1021/acs.iecr.0c05432
25. Lebedev OV, Tikunova EP, Golubev EK, et al. Solid-State Processing of Nascent Disentangled UHMWPE Reactor Powders Mixed with Carbon Nanoparticles. Macromolecular Symposia. 2024; 413(4). doi: 10.1002/masy.202400008
26. Christakopoulos F, Busato SP, Kong X, et al. Solid-state extrusion of nascent disentangled ultra-high molecular weight polyethylene. Polymer Engineering & Science. 2024; 64(8): 3606-3616. doi: 10.1002/pen.26787
27. Li L, Kong F, Xiao A, et al. Constructing polyolefin-based lithium-ion battery separators membrane for energy storage and conversion. Energy Storage and Conversion. 2024; 2(4): 1631. doi: 10.59400/esc1631
28. Tang X, Xing J, Yan X, et al. Metallocene Polyolefins Reinforced by Low-Entanglement UHMWPE through Interfacial Entanglements. Advances in Polymer Technology; 2022. doi: 10.1155/2022/9344096
29. Tao G, Chen Y, Mu J, et al. Exploring the entangled state and molecular weight of UHMWPE on the microstructure and

mechanical properties of HDPE/UHMWPE blends. Journal of Applied Polymer Science. 2021; 138(30). doi: 10.1002/app.50741
30. Vadivel HS, Bek M, Šebenik U, et al. Do the particle size, molecular weight, and processing of UHMWPE affect its thermomechanical and tribological performance?. Journal of Materials Research and Technology. 2021; 12: 1728-1737. doi: 10.1016/j.jmrt.2021.03.087
31. Chen Y, Liang P, Yue Z, et al. Entanglement Formation Mechanism in the POSS Modified Heterogeneous Ziegler–Natta Catalysts. Macromolecules. 2019; 52(20): 7593-7602. doi: 10.1021/acs.macromol.9b00610
32. Wang Z, Li B, Christakopoulos F, et al. Structure Formation and Unexpected Ultrafast Re-entanglement Dynamics of Disentangled Ultrahigh Molecular Weight Polyethylene. Macromolecules. 2024; 57(21): 10240-10252. doi: 10.1021/acs.macromol.4c01733
33. Ye C, Yang T, Li Z, et al. Novel determining technique for the entanglement degree of ultra-high molecular weight polyethylene. Materials Letters. 2023; 349: 134783. doi: 10.1016/j.matlet.2023.134783
34. Hawke LGD, Romano D, Rastogi S. Nonequilibrium Melt State of Ultra-High-Molecular-Weight Polyethylene: A Theoretical Approach on the Equilibrium Process. Macromolecules. 2019; 52(22): 8849-8866. doi: 10.1021/acs.macromol.9b01152
35. Oleynik IV, Shundrina IK, Oleyinik II. Highly active titanium(IV) dichloride FI catalysts bearing a diallylamino group for the synthesis of disentangled UHMWPE. Polymers for Advanced Technologies. 2020; 31(9): 1921-1934. doi: 10.1002/pat.4917
36. Yao Y, Jiang S, Rastogi S. 13C Solid State NMR Characterization of Structure and Orientation Development in the Narrow and Broad Molar Mass Disentangled UHMWPE. Macromolecules. 2014; 47(4): 1371-1382. doi: 10.1021/ma402232c
37. Chen L, Deng B, Li X, et al. Structural evolution of UHMWPE gel fibers as high degree plasticized system during stretching: An in-situ wide and small angle X-ray scattering study. Polymer. 2022; 255: 125149. doi: 10.1016/j.polymer.2022.125149
38. Litvinov VM, Xu J, Melian C, et al. Morphology, Chain Dynamics, and Domain Sizes in Highly Drawn Gel-Spun Ultrahigh Molecular Weight Polyethylene Fibers at the Final Stages of Drawing by SAXS, WAXS, and 1H Solid-State NMR. Macromolecules. 2011; 44(23): 9254-9266. doi: 10.1021/ma201888f
39. Li X, Mao Y, Ma H, et al. An in-situ X-ray scattering study during uniaxial stretching of ionic liquid/ultra-high molecular weight polyethylene blends. Polymer. 2011; 52(20): 4610-4618. doi: 10.1016/j.polymer.2011.07.034
40. Sharma A, Kruteva M, Willner L, et al. SANS and SAXS Investigation of the Melt State Structure in Disentangled Ultrahigh Molecular Weight Polyethylene. ACS Macro Letters. 2025; 14(3): 349-353. doi: 10.1021/acsmacrolett.5c00100
41. Wu SL, Qiao J, Guan J, et al. Nascent disentangled UHMWPE: Origin, synthesis, processing, performances and applications. European Polymer Journal. 2023; 184: 111799. doi: 10.1016/j.eurpolymj.2022.111799
42. Gote RP, Zhao J, Romano D, et al. Solid-State Processing of In Situ Blended Prepolymer with Z–N Synthesized UHMWPE: Role of the Prepolymer. Macromolecules. 2025; 58(7): 3604-3621. doi: 10.1021/acs.macromol.4c03097
43. Chen J, Qu S, Li X, et al. Single-Site Catalyst for the Synthesis of Disentangled Ultra-High-Molecular-Weight Polyethylene. Polymers. 2025; 17(1): 95. doi: 10.3390/polym17010095
44. Matsui S, Fujita T. FI Catalysts: super active new ethylene polymerization catalysts. Catalysis Today. 2001; 66(1): 63-73. doi: 10.1016/S0920-5861(00)00605-2
45. Makio H, Fujita T. Development and Application of FI Catalysts for Olefin Polymerization: Unique Catalysis and Distinctive Polymer Formation. Accounts of Chemical Research. 2009; 42(10): 1532-1544. doi: 10.1021/ar900030a
46. Li W, Yang H, Zhang J, et al. Immobilization of isolated FI catalyst on polyhedral oligomeric silsesquioxane-functionalized silica for the synthesis of weakly entangled polyethylene. Chemical Communications. 2016; 52(74): 11092-11095. doi: 10.1039/c6cc04814e
47. Bogdos MK, Stepanović O, Bismuto A, et al. Mechanistically informed selection rules for competing β-hydride and β-heteroatom eliminations. Nature Synthesis. 2022; 1(10): 787-793. doi: 10.1038/s44160-022-00145-x
48. Li K, Zhou H, Qin Y, et al. ω-Alkenylmethyldichlorosilane-assisted propylene polymerization with Ziegler-Natta catalyst to long chain-branched polypropylene. Polymer. 2020; 202: 122737. doi: 10.1016/j.polymer.2020.122737
49. Mirabi B, Lautens M, Baik MH. The rhodium riddle: computational insights into competitive β-hydride vs. β-fluoride elimination. Catalysis Science & Technology. 2025; 15(8): 2482-2492. doi: 10.1039/d4cy01495b
50. Patel K, Chikkali SH, Sivaram S. Ultrahigh molecular weight polyethylene: Catalysis, structure, properties, processing and

applications. Progress in Polymer Science. 2020; 109: 101290. doi: 10.1016/j.progpolymsci.2020.101290
51. Kawai K, Fujita T. Discovery and Development of FI Catalysts for Olefin Polymerization: Unique Catalysis and Distinctive Polymer Formation. Springer Berlin Heidelberg: Berlin, Heidelberg; 2009.
52. Makio H, Terao H, Iwashita A, et al. FI Catalysts for Olefin Polymerization—A Comprehensive Treatment. Chemical Reviews. 2011; 111(3): 2363-2449. doi: 10.1021/cr100294r
53. Fujita T, Kawai K. FI Catalysts for Olefin Oligomerization and Polymerization: Production of Useful Olefin-Based Materials by Unique Catalysis. Topics in Catalysis. 2014; 57(10-13): 852-877. doi: 10.1007/s11244-014-0246-z
54. Damavandi S, Samadieh N, Ahmadjo S, et al. Novel Ni-based FI catalyst for ethylene polymerization. European Polymer Journal. 2015; 64: 118-125. doi: 10.1016/j.eurpolymj.2014.12.032
55. Makio H, Kashiwa N, Fujita T. FI Catalysts: A New Family of High Performance Catalysts for Olefin Polymerization. Advanced Synthesis & Catalysis. 2002; 344(5): 477-493. doi: 10.1002/1615-4169(200207)344:5<477::AID-ADSC477>3.0.CO;2-6
56. Sandaroos R, Zohuri GH, Ahmadjo S, et al. FI Catalyst for Polymerization of Olefin. In: Polymerization. IntechOpen: Rijeka; 2012.
57. Yang H, Lolage S, van der Eem J, et al. Silica-supported catalyst for the synthesis of low entangled UHMWPE suitable for solid-state processing. Molecular Catalysis. 2024; 552: 113668. doi: 10.1016/j.mcat.2023.113668
58. Ni Q, Chen M, Chen Y, et al. Suppressing the Entanglements of Ultrahigh-Molecular-Weight Polyethylene via Controlling the Adhesion Effect in a POSS-Modified Support. Industrial & Engineering Chemistry Research. 2022; 61(19): 6367-6374. doi: 10.1021/acs.iecr.2c00566
59. Zhou J, Zhang X, Zhao S, et al. Study on the effects of soluble POSS on chain disentanglement in UHMWPE polymerization. Polymer. 2022; 244: 124561. doi: 10.1016/j.polymer.2022.124561
60. Zhou J, Zhang X, Zhao S, et al. Chain disentanglement in POSS/UHMWPE composites prepared via in-situ polymerization. Journal of Polymer Research. 2022; 29(3). doi: 10.1007/s10965-022-02909-7
61. Zhang X, Zhao S, Xin Z. The chain dis-entanglement effect of polyhedral oligomeric silsesquioxanes (POSS) on ultra-high molecular weight polyethylene (UHMWPE). Polymer. 2020; 202: 122631. doi: 10.1016/j.polymer.2020.122631
62. Zhang Z, Jiang B, He F, et al. Comparative Study on Kinetics of Ethylene and Propylene Polymerizations with Supported Ziegler–Natta Catalyst: Catalyst Fragmentation Promoted by Polymer Crystalline Lamellae. Polymers. 2019; 11(2): 358. doi: 10.3390/polym11020358
63. Moeini N, Teimoury H, Salimi M, et al. Influence of the reaction conditions on the Ziegler-Natta catalyzed ethylene polymerization: Kinetics and properties of the resulting polymers. Polymer. 2024; 293: 126640. doi: 10.1016/j.polymer.2023.126640
64. Abedi S, Abdouss M. A review of clay-supported Ziegler–Natta catalysts for production of polyolefin/clay nanocomposites through in situ polymerization. Applied Catalysis A: General. 2014; 475: 386-409. doi: 10.1016/j.apcata.2014.01.028
65. Liu K, de Boer EL, Yao Y, et al. Heterogeneous Distribution of Entanglements in a Nonequilibrium Polymer Melt of UHMWPE: Influence on Crystallization without and with Graphene Oxide. Macromolecules. 2016; 49(19): 7497-7509. doi: 10.1021/acs.macromol.6b01173
66. Bhajiwala H, Gupta V. External donor modified Mg-Ti based Z-N catalyst system for synthesis of Ultrahigh molecular weight polyethylene. Polymer. 2023; 289: 126483. doi: 10.1016/j.polymer.2023.126483
67. Nakayama Y, Bando H, Sonobe Y, et al. Development of Single-Site New Olefin Polymerization Catalyst Systems Using MgCl2-Based Activators: MAO-Free MgCl2-Supported FI Catalyst Systems. Bulletin of the Chemical Society of Japan. 2004; 77(4): 617-625. doi: 10.1246/bcsj.77.617
68. Bahri-Laleh N, Ghavampoor AH, Karkhaneh F. Ethylene polymerization with homogeneous catalysts. Homogeneous Polymerization and Oligomerization Reactions; 2025. doi: 10.1016/b978-0-443-15680-9.00009-0
69. Gote RP, Romano D, van der Eem J, et al. Unprecedented Mechanical Properties in Linear UHMWPE Using a Heterogeneous Catalytic System. Macromolecules. 2022; 56(1): 361-378. doi: 10.1021/acs.macromol.2c02215
70. Ronca S, Romano D, Forte G, et al. Improving the performance of a catalytic system for the synthesis of ultra high molecular weight polyethylene with a reduced number of entanglements. Advances in Polymer Technology. 2012; 31(3): 193-204. doi: 10.1002/adv.21265
71. Romano D, Tops N, Andablo-Reyes E, et al. Influence of Polymerization Conditions on Melting Kinetics of Low Entangled UHMWPE and Its Implications on Mechanical Properties. Macromolecules. 2014; 47(14): 4750-4760. doi:

10.1021/ma5008122

72. Romano D, Andablo-Reyes E, Ronca S, et al. Aluminoxane co-catalysts for the activation of a bis phenoxyimine titanium (IV) catalyst in the synthesis of disentangled ultra-high molecular weight polyethylene. Polymer. 2015; 74: 76-85. doi: 10.1016/j.polymer.2015.07.039
73. Lemstra PJ, Smith P. Ultra-drawing of High Molecular Weight Polyethylene. British Polymer Journal. 1980; 12(4): 212-214. doi: 10.1002/pi.4980120415
74. Smith P, Lemstra PJ. Ultra-high strength polyethylene filaments by solution spinning/drawing. 3. Influence of drawing temperature. Polymer. 1980; 21(11): 1341-1343. doi: 10.1016/0032-3861(80)90205-0
75. Smith P, Lemstra PJ. Ultra-high-strength polyethylene filaments by solution spinning/drawing. Journal of Materials Science. 1980; 15(2): 505-514. doi: 10.1007/bf02396802
76. Pandey A, Champouret Y, Rastogi S. Heterogeneity in the Distribution of Entanglement Density during Polymerization in Disentangled Ultrahigh Molecular Weight Polyethylene. Macromolecules. 2011; 44(12): 4952-4960. doi: 10.1021/ma2003689
77. Forte G, Ronca S. Synthesis of Disentangled Ultra-High Molecular Weight Polyethylene: Influence of Reaction Medium on Material Properties. International Journal of Polymer Science. 2017; 2017: 1-8. doi: 10.1155/2017/7431419
78. Rastogi S, Yao Y, Ronca S, et al. Unprecedented High-Modulus High-Strength Tapes and Films of Ultrahigh Molecular Weight Polyethylene via Solvent-Free Route. Macromolecules. 2011; 44(14): 5558-5568. doi: 10.1021/ma200667m
79. Talebi S, Duchateau R, Rastogi S, et al. Molar Mass and Molecular Weight Distribution Determination of UHMWPE Synthesized Using a Living Homogeneous Catalyst. Macromolecules. 2010; 43(6): 2780-2788. doi: 10.1021/ma902297b
80. Li W, Chen T, Guan C, et al. Influence of Polyhedral Oligomeric Silsesquioxane Structure on the Disentangled State of Ultrahigh Molecular Weight Polyethylene Nanocomposites during Ethylene in Situ Polymerization. Industrial & Engineering Chemistry Research. 2015; 54(5): 1478-1486. doi: 10.1021/ie504273r
81. Li W, Guan C, Xu J, et al. Disentangled UHMWPE/POSS nanocomposites prepared by ethylene in situ polymerization. Polymer. 2014; 55(7): 1792-1798. doi: 10.1016/j.polymer.2014.02.023
82. Chen T, Yang H, Li W. Phase structure and mechanical properties of disentangled ultra-high molecular weight polyethylene/polyhedral oligomeric silsesquioxane nanocomposites in a solid state. Journal of Polymer Research. 2015; 22(11). doi: 10.1007/s10965-015-0867-3
83. Wang Y, Wu SL. Deciphering the role of FI catalyst's C substituent on the non-isothermal crystallization kinetics of nascent disentangled UHMWPE. Materials Today Communications. 2024; 41: 110244. doi: 10.1016/j.mtcomm.2024.110244
84. Wang Y, Fan H, Li B. UHMWPE with short-chain branches synthesized by alkenyl substituted phenoxy–imine catalysts in ethylene polymerization. Journal of Polymer Science Part A: Polymer Chemistry. 2016; 54(24): 3808-3818. doi: 10.1002/pola.28265