Review

Preparation of nascent disentangled ultra-high molecular weight polyethylene based on Ziegler-Natta catalyst

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Abstract: Ziegler-Natta (Z-N) catalysts hold great significance in the industrial production of ultrahigh molecular weight polyethylene (UHMWPE), given that their outstanding efficacy, profound impact on the molecular weight (MW) of UHMWPE, and extensive industrial applications are highly conspicuous. However, the UHMWPE prepared by Z-N catalyst is usually highly entangled. Considering chain entanglement is essential for altering the processability and mechanical characteristics of nascent UHMWPE, the synthesis of disentangled UHMWPE (dis-UHMWPE) is essential for industrial scalability, therefore holding considerable practical importance. This review summarized recent progress in optimizing Z-N catalysts for the synthesis of dis-UHMWPE, providing a comprehensive overview of research advancements, clarifying polymerization settings, linking polymer structure and activity, and introducing design principles for polymerization techniques. Moreover, the overarching objective is to reveal the principles behind material preparation methods and potentiate the application prospects of UHMWPE materials, therein propelling the advancement of related fields.

Keywords: UHMWPE; Ziegler-Natta catalyst; polymerization; disentanglement

1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) is increasingly preferred by numerous industries due to its semi-crystalline structure and exceptional mechanical qualities, including impact strength, wear resistance, low friction coefficient, chemical resistance, and low dielectric constant [1,2]. Consequently, it has been utilized in various domains, including cables, robust ropes, ballistic jackets, tissue engineering scaffolds, and prosthetic joints [3–8]. Currently, the manufacturing of commercial UHMWPE (C-UHMWPE) predominantly use the Ziegler Natta (Z-N) catalyst and the ethylene slurry polymerization method [9]. Nevertheless, the Z-N catalyst possesses numerous active sites that are randomly dispersed around the carrier's surface and are in proximity to one another. The polymerization process results in substantial overlap of polymer chains at neighboring active sites, causing entanglement of molecular chains, which restricts their mobility and adversely impacts mechanical and processing capabilities [10]. The elevated molecular weight (MW) leads to significant entanglement of UHMWPE molecular chains, resulting in a low critical shear rate and challenges in flow and processing.

Notably, the relaxation of highly entangled polymer chains during the production process is extremely sluggish [11]. The UHMWPE melt exhibits high viscosity and restricted fluidity, making it difficult to dissolve in most solvents even

at elevated temperatures [11]. Specifically, when the shear rate exceeds its low critical value, UHMWPE melts experience melt fracture during screw extrusion or conventional melt mixing [12]. Moreover, in powder sintering, the appropriate temperature, pressure, and time durations are essential for polymer chains to migrate between powder particles [13–15]. Consequently, ram-extruded or compression-molded UHMWPE often retains a memory of the original particles in the form of grain boundary defects related to high entanglement, which can act as potential sources for the initiation of fatigue cracks, abrasive wear, and ultimate failure [16]. To address this challenge, numerous attempts have been made to improve the processability and consolidation degree of UHMWPE [17]. For instance, adding low MW polyethylene or liquid paraffin as processing aids [18,19]. However, this gives rise to a partial or substantial attenuation of the advantageous properties of UHMWPE, which is attributed to the dilution effect of the low MW component and the shear degradation within the extruder [20]. Conventional processing methods like extrusion, blown film, and injection molding are highly challenging for UHMWPE, severely restricting its application range [11]. Therefore, the preparation of nascent disentangled UHMWPE (dis-UHMWPE) is of crucial significance. Notably, by modifying the support, Z-N catalysts with active centers segmented by isolators can be obtained, which enables the in-situ generation of dis-UHMWPE during chain propagation (**Figure 1**) [21,22].
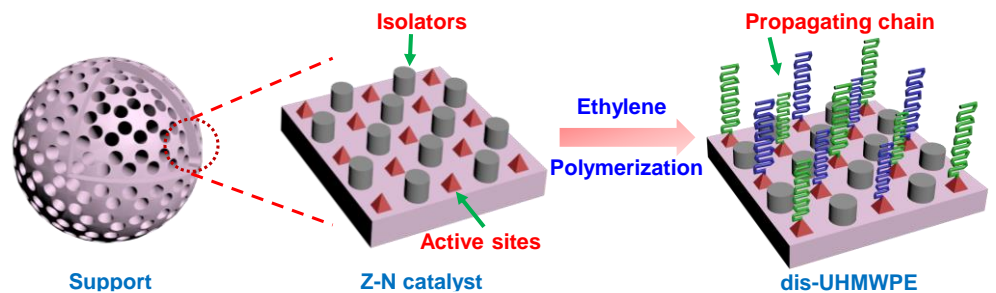

Figure 1. A typical schematic illustration of the dis-UHMWPE synthesis mechanism based on the Z-N catalyst.

In comparison to commercially available C-UHMWPE, dis-UHMWPE exhibits a reduced number of entanglement nodes in molecular chains, resulting in enhanced processability and creating new opportunities for the production, processing, and application of UHMWPE materials [23]. The substantial commercial potential has garnered significant interest from both academics and industry. Chain entanglement regulation can be primarily accomplished through polymerization techniques such as catalyst design [24], blending modification [25], or the utilization of solvents and force fields for disentanglement during downstream processing [10]. However, although chain entanglement can be regulated during the blending or processing stages, numerous industrial issues remain, including elevated production costs, enhanced processing complexity, and decreased product performance. Significantly, polymerization methods have gain more attention on synthesizing UHMWPE with enhanced flow and drawability characteristics [26]. Consequently, it is essential to formulate strategies for polymerization methods (such as optimizing polymerization conditions and catalyst design) to acquire the preparation technology for nascent

low-entanglement UHMWPE, with catalyst technology being the core [27]. For example, ethylene polymerization occurs under specific conditions of separated active sites or low temperatures for crystallization, a single nascent polymer chain can solidify without overlapping with others, thus forming dis-UHMWPE [28]. Besides, polymerization using a diluted catalyst could ensure sufficient spatial distance between the growing alkyl chains, permitting the chains to crystallize independently upon formation [10,29].

Notably, Z-N catalysts are crucial in the manufacture of UHMWPE due to their outstanding effectiveness, significant impact on the structure and property of UHMWPE, and numerous industrial prospects. Concurrently, considering chain entanglement is essential for modulating the processability and mechanical characteristics of nascent UHMWPE, the synthesis of dis-UHMWPE through Z-N catalyst polymerization is vital for both theoretical research and industrial applications. In this regard, we have comprehensively summarized the recent progress in optimizing Z-N catalysts and their associated polymerization systems for the synthesis of disentangled UHMWPE, compromising a detailed overview of research developments, the relationships between polymerization conditions and polymer structure, and the design concepts of polymerization methods. Overall, this summary is committed to furnish valuable reference and design inspiration to researchers in related to dis-UHMWPE characterization and synthesis, thereby promoting further advancements in this domain.

2. Characterization method for entanglement of UHMWPE

2.1. Melt rheological method

The melt rheological characterization method employs the dynamic time sweep mode of a rotational rheometer. PE is heated to a temperature of 160 °C, at which the molten UHMWPE displays a gel-like consistency with limited flowability [29]. At a constant scanning test frequency of 0.5 Hz, within the linear viscoelastic region of PE, the molecular chain segments undergo relatively fast movements and re-entanglement due to elevated thermal motion. As the entanglement phenomenon intensifies and the density of entanglement points increases, the storage modulus (G') of the polyethylene melt gradually increases and eventually reaches a thermodynamic equilibrium state, referred to as the thermodynamic equilibrium modulus, denoted as $G_N(0)$. Two indications are frequently utilized as analytical constants for evaluating the extent of chain entanglement. Firstly, the $G_N(t)$ value ($G_N(t) = G'(t)/G'(\text{max})$, where $G'(t)$ signifies the elastic modulus at a given time (t) and $G'(\text{max})$ indicates the thermodynamic maximum modulus) functions as a metric to assess the extent of chain entanglement [29]. An increased value of $G_N(t)$ signifies a heightened density of chain entanglement in the polymer melt and a reduced entanglement molecular weight (M_e). Secondly, the time (t_m) for the PE to reach 98% of the relative thermodynamic equilibrium modulus (i.e., $G_N(0)$) is employed as an additional parameter **(Figure 2)**. An extended t_m results in increased time for the chain segments to attain thermodynamic equilibrium, indicating a reduced level of chain entanglement in the nascent PE.

Notably, based on the thermodynamic equilibrium formula (i.e., $G_N(0) = $

$g_n \rho RT/M_e$, where $G_N(0)$ represents the equilibrium modulus, g_n is a numerical factor valued at either 1 or 4/5, ρ denotes density, R signifies the gas constant, T indicates thermodynamic temperature), the $G_N(0)$ of UHMWPE remains constant (~2.0 MPa) at a specific temperature. Notably, to maintain the pristine chain entanglement structure of nascent polyethylene during the initial stage of the melt rheological method, sample preparation through compression molding must be conducted below the melting point (T_m). This constraint renders it infeasible to mold many nascent PE with a substantial amount of entanglement, thus imposing limitations on the accuracy of analytical methods. Nevertheless, this method remains the most prevalent approach in the field [30].
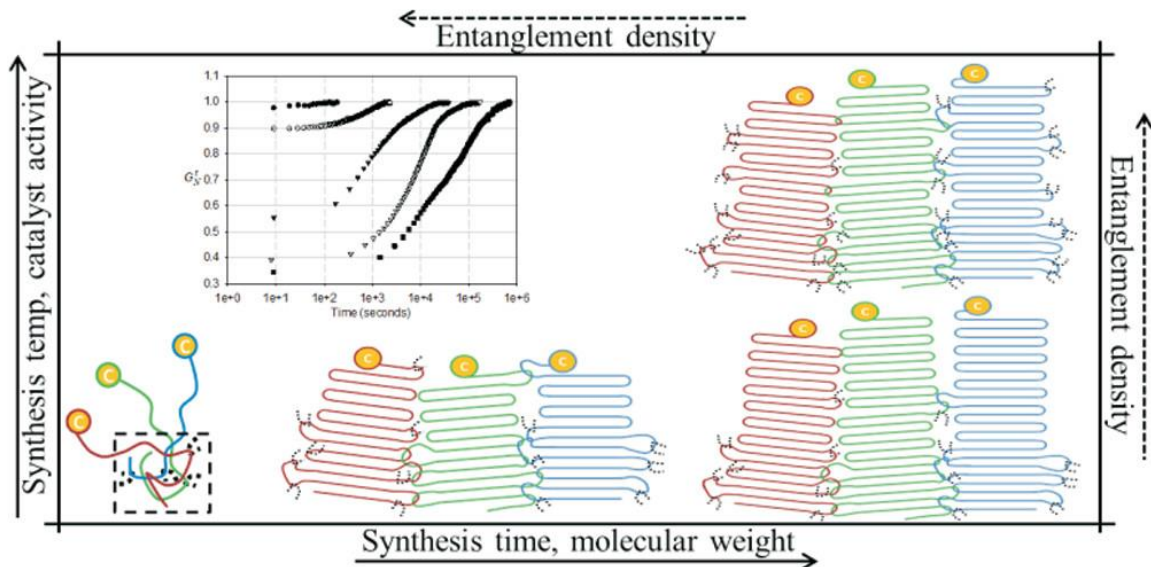

Figure 2. Schematic illustration of the melt rheological method for entanglement characterization of dis-UHMWPE. Reprinted with permission from reference [29], copyright American Chemical Society 2011.

2.2. Thermodynamic annealing method

The thermodynamic annealing characterization utilizes a differential scanning calorimeter (DSC) to control the melting and crystallization behavior of UHMWPE at different temperatures, allowing for the assessment of the extent of chain entanglement in polyethylene. This method primarily encompasses two modes, namely heating melting annealing and cooling crystallization annealing [31]. During the heating melting annealing mode, the program involves conducting annealing experiments at a temperature 5 °C–8 °C below the T_m of UHMWPE. For instance, during the annealing process at 136 °C, the crystals formed by the arrangement of native disentangled polyethylene segments cannot melt, leading to the retention of primary flakes [32]. Meanwhile, polyethylene molecular chains in the entangled and amorphous regions (including those in the entangled or disentangled amorphous regions) will detach and melt from the surface of the flakes. During the cooling crystallization process, the molten segments will rearrange to form crystal regions, resulting in the appearance of two different melting peaks in the final DSC curve [33]. In the amorphous region, a higher degree of entanglement leads to fewer molecular chains peeling off from the crystal surface during annealing, resulting in a smaller low-temperature peak in the final DSC melting curve. Thus, the normalized

ratio of low-temperature peak area to the sum of low-temperature and high-temperature peak areas can be used to measure the polyethylene chain entanglement degree, where a higher value implies a higher degree of disentanglement.

On the other hand, the cooling crystallization annealing mode adopts high-temperature annealing at 160 °C, where the polyethylene segments become entangled at high temperature and are then cooled to ~128 °C for crystallization annealing [34]. During this process, two types of crystal regions could form, one during the cooling process and the other during the 128 °C annealing process. Correspondingly, two different melting peaks usually appear in the DSC curve. A reduced degree of chain entanglement in nascent polyethylene could result in an increased formation of crystalline areas during the crystallization annealing process, leading to a larger high-temperature peak area in the final DSC curve. Recently, Ye et al. [35] have established a method for characterizing the entanglement degree of UHMWPE by comparing low entanglement standard samples with corresponding products using DSC. The quantitative value related to the degree of entanglement of UHMWPE (C_{tan}) value calculated by this method is directly proportional to the traditional rheological entanglement number (Z), which verifies the accuracy of this method and resolves the deviation in entanglement measurement caused by an inaccurate platform modulus in the rheological testing process of low MW polyethylene. This method not only obtain entanglement information of resins and products with a MW exceeding 1.5 × 105 g/mol, but also does not require the use of extremely high temperatures, thus avoiding problems such as molecular chain degradation.

2.3. Solid NMR method

The solid NMR characterization method is based on the aggregated crystal phase structure in UHMWPE solids to measure the degree of chain entanglement. Specifically, Yao et al. [31] conducted qualitative scanning of solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ^{13}C-NMR) on UHMWPE samples with varying entanglement degrees. The results showed that in low-entanglement samples, the monoclinic signal intensity at 32 ppm increased significantly as the temperature decreased. However, this characteristic peak was not observed in high-entanglement samples. The enhancement of the monoclinic crystal peak is attributed to the lower density of entanglement points in low-entangled samples. These points, being intermediate phase segments between crystalline and amorphous phases could facilitate the formation of monoclinic crystal phases during cooling. Furthermore, they used the single pulse-magic angle spinning (SP/MAS) NMR mode for quantitative characterization of the crystal phase composition in UHMWPE solids, enabling a more accurate analysis of the chain entanglement degree (**Figure 3**). Furthermore, Li et al. [36] established that low-field solid-state NMR is a practical and efficient technique for investigating the entangled structure of nascent UHMWPE through chain dynamics. The free induction decay (FID) curves of UHMWPE can be modeled using two components corresponding to the crystalline and amorphous

phases. The UPEN multi-exponential inversion program is effective for evaluating relaxation time distributions, while the Carr-Purcell-Meiboom-Gill (CPMG) echo can selectively filter the crystalline phase signal. The transverse relaxation durations (T_2) distribution in less entangled UHMWPE is heterogeneous (double peak), in contrast to the single peak observed in commercially available highly entangled UHMWPE. A wide longitudinal relaxation time (T_1) distribution is evident in embryonic less entangled UHMWPE, signifying a diverse distribution of entangled sites. Moreover, heating nascent UHMWPE below the T_m may induce chain rearrangement and recrystallization, contingent upon the original entangled configuration.
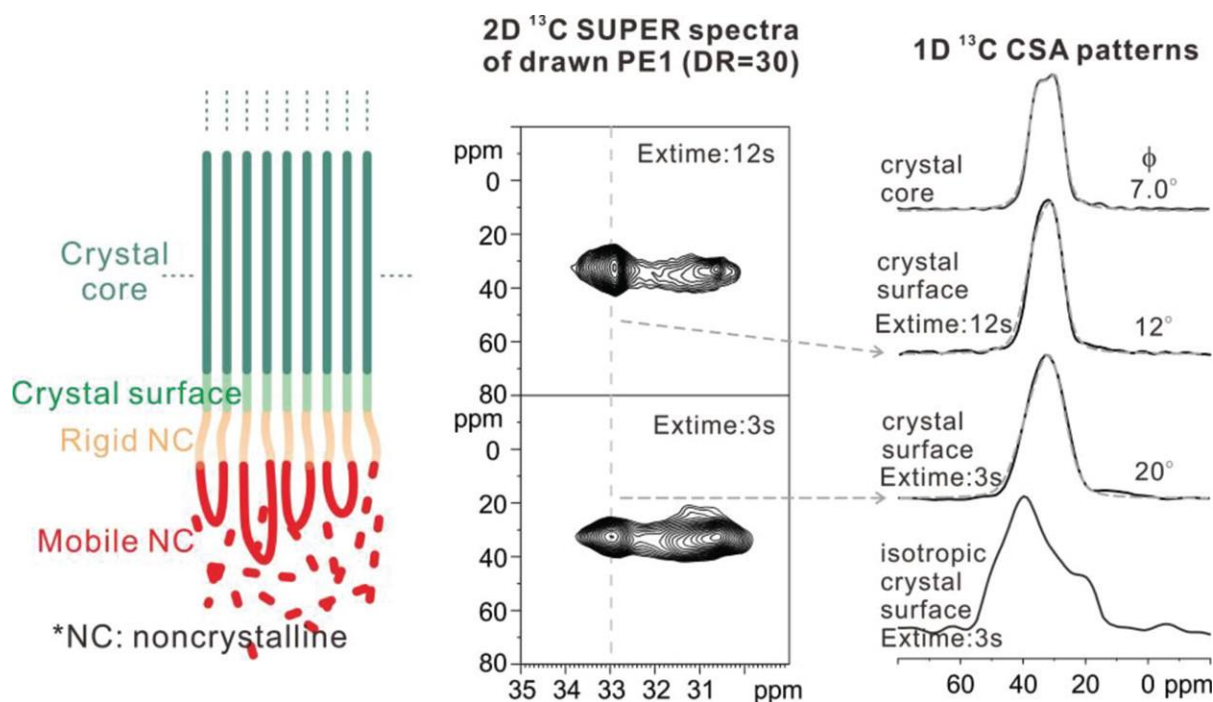

Figure 3. 2D SP-SUPER and CP-SUPER spectra of the UHMWPE sample. Reprinted with permission from reference [31], copyright American Chemical Society 2014.

Recently, Zhao et al. [37] synthesized partially disentangled UHMWPE using freeze-extraction and investigated the improvement of chain mobility. A low-field solid-state NMR with a completely refocused ^{1}H free induction decay (FID) can discern variations in chain segmental mobility during the melting of UHMWPE with varying degrees of entanglement. UHMWPE chains with longer chains were more challenging to combine into mobile segments after detaching from the lamellae crystalline during melting. Furthermore, ^{1}H double quantum (DQ) NMR was employed to extract information from residual dipolar interactions. The DQ peak manifested earlier in intramolecular-nucleated UHMWPE due to robust crystalline restrictions before melting. During melting, the less-entangled UHMWPE remained disentangled, whereas the less-entangled high-density polyethylene (HDPE) did not. Nonetheless, no significant differences were observed in DQ studies for UHMWPE melts with varying degrees of entanglement post-melting, which is attributed to the minimal impact of entanglements compared to the overall residual dipolar interaction

in the melts. Overall, the less-entangled UHMWPE could maintain its disentangled state near the melting point long enough for better processing.

3. Recent advances of dis-UHMWPE synthesis using Z-N catalyst

Polymerization methods for synthesizing UHMWPE with improved flow and drawability have received increased attention. Thus, formulating strategies for polymerization methods (e.g., catalyst design and optimizing conditions) is essential to obtain the technology for preparing nascent dis-UHMWPE (**Table 1**). For example, during ethylene polymerization under conditions of separated active sites or low crystallization temperatures, a single nascent chain can solidify without overlap, forming dis-UHMWPE. Also, using a diluted catalyst ensures sufficient spatial separation for independent crystallization of growing alkyl chains. Notably, polyhedral oligomeric silsesquioxane (POSS) are gaining more and more attention during dis-UHMWPE preparation using Z-N catalyst.

Table 1. Summary of representative dis-UHMWPE product using modified Z-N catalyst discussed in this review.

Catalyst	Cocatalyst	Activity (10^6 g PE·mol^{-1}[Ti]·h^{-1})	MW (10^6 g/mol)	MWD	T_m^1 (°C)	X_c^1 (%)	T_m^2 (°C)	X_c^2 (%)	Ref.
POSS-1.89	TEA	14.2	2.8	6.0	136.09	53.89	120.38		[38]
Cat-POSS-20	TEA	1.3	2.05	9.5	144.2	65.5	137.2	53.3	[39]
POSS-10%-cat	TiBA	2.7	2.25	11.8	143.8	66.9	137	51	[40]
Cat-POSS-30%	TEA	3.52	1.42	6.17					[41]
0.2% POSS	TEA	11.81	2.6	5.9	140.2	66.89	135.8	49.64	[42]
4POSS-Cat	TEA	6.052	2.46	5.0	144.3	66.9	136.8	50.4	[43]
TiCl$_4$/OH-POSS/sup-1	TEA	18.83	1.53	7.2	136.55	62.16	119.79		[44]
SiO$_2$/4%PS	TEA	3.1	2.63		144.2	66.5	138.8	47.2	[45]
PA-Cat-2.0	TEA		5.3		142.9	75	135.4	58	[46]
TiCl$_4$/MgCl$_2$		2.4	1.46	4.3	142.6	66	135.6	47.2	[47]

3.1. Modified Z-N catalyst based on POSS

POSS nanoparticles are hybrid materials comprising stiff silicon inorganic cores modified with organic groups [48]. More than 100 distinct POSS compounds, each with unique organic functional groups, are available for commercial use. These nanoparticles have gained significant attention due to their small size, measuring only 1.5 nm, making them the tiniest silica particles [49]. Their physical dimensions are relatively substantial compared to polymer sizes, almost matching the dimensions of most polymer segments and coils [50]. Reports indicate that nanoparticles smaller than the entanglement mesh widths can facilitate chain disentanglement and accelerate monomeric relaxation rates [51]. Recently, several studies have further examined the impact of POSS on the molecular mobility of polymers, which is believed to be associated with disentanglement [52–54]. Nevertheless, attaining a deeper comprehension of the influence of POSS on the entanglement of UHMWPE during Z-N polymerization continues to pose a challenge. Zhou et al. [38] incorporated POSS into UHMWPE composites using

in-situ ethylene polymerization at 85 °C, utilizing an Al: Ti ratio of 150. The influence of POSS integration on the polymerization kinetics, melt viscosity, thermal transitions, annealing characteristics, and mechanical strength of UHMWPE was thoroughly studied. The disentangling performance was enhanced by incorporating varying concentrations of POSS, ranging from 0.5 to 2.16 wt%. This may be due to increased dispersion and less POSS aggregation, which served as a barrier and expanded the molecular weight distribution (MWD), hence improving processability. Subsequent analysis revealed that the determined activation energy for the pure UHMWPE and POSS/UHMWPE nanocomposites was 550.31 ± 72.60 kJ/mol and 303.37 ± 27.71 kJ/mol, respectively. Furthermore, low concentrations of POSS (0.23–1.89 wt‰) may lead to reduced melt viscosities, whereas elevated concentrations result in increased viscosity. The incorporation of POSS significantly reduced the rubbery plateau modulus of UHMWPE, indicating a dilatation effect on polymer entanglements. The in-situ approach is particularly effective in minimizing the additives required.

Li et al. [39] introduced a POSS-modified Z-N catalyst for the production of weakly entangled UHMWPE at high temperatures with considerable efficacy. They found that the integration of POSS could generate ~48 nm nano-aggregates sticking to SiO_2 surfaces, which is essential for the production of dis-UHMWPE. Experimental and computational data further validated the nanoaggregate structure, in which a single POSS molecule can coordinate multiple $MgCl_2$ molecules as electrical donors to immobilize $TiCl_4$. Consequently, the catalyst compromised two active domains inside the POSS/$MgCl_2$ nanoaggregates and δ-$MgCl_2$, respectively. The former displayed negligible activity in ethylene polymerization, serving as horizontal barriers that isolate active $TiCl_4$ sites and facilitate chain extension. Therefore, the reduction in entanglement may stem from the steric hindrance induced by $MgCl_2$/POSS nanoaggregates, which could enlarge the spatial separation between extended chains and curtails chain overlapping. Consequently, this catalyst shown remarkable activity (i.e. 1.3×10^6 g PE·mol^{-1}[Ti]·h^{-1}·bar^{-1}) for the production of weakly entangled polyethylene at 60 °C. Furthermore, substituting macro-SiO_2 with pore-restricted commercial silica (i.e., Grace-955 SiO_2) could preserve the barrier function, facilitating the synthesis of weakly entangled UHMWPE with an increased molecular weight (2.9×10^6 g/mol) and enhanced activity (4.5×10^6 g PE·mol^{-1}[Ti]·h^{-1}·bar^{-1}). Chen et al. [40] utilized a Z-N catalyst modified with POSS/$MgCl_2$ nanoaggregates as horizontal spacers between active sites to create UHMWPE with less entanglement, indicating that the entanglement density of nascent UHMWPE can be regulated by modifying polymerization conditions prior to particle fragmentation (**Figure 4**). The delicately modified double hydroxides on POSS could increase the binding energy of Mg 2p and Ti(IV) 2p in these nanoaggregates, reducing their ethylene polymerization efficiency. Moreover, POSS/$MgCl_2$ nanoaggregates can separate adjacent polymer chains due to their higher dimensionality than the expected chain folded length. Meanwhile, UHMWPE production with activity levels of 2.7×10^6 g PE·mol^{-1}[Ti]·h^{-1} was achieved at 60-85 °C utilizing the POSS-modified Z-N catalyst with triisobutylaluminum (TiBA) cocatalyst. Notably, the critical importance of nanoaggregate separation could maintain particle integrity, thus diminishing the creation of entanglements. Besides,

the $G_N(0)$ is employed to identify variations in entanglement density among synthesized UHMWPE. In the elastic modulus build-up curves, the $G_N(0)$ increment equation for UHMWPE at 30 min was $1.052 \times A^{0.15609}$ (where A represents polymerization activity), whereas at 60 min it was $2.44 \times A^{0.07117}$. Further investigation indicated that the density of nascent UHMWPE entanglement decreases exponentially with increasing nanoaggregate concentration. Significantly, $G_N(0)$ exhibited a nearly exponential decline with the increase in activity when the POSS loading reaches 10 wt %. This suggested that POSS/MgCl2 nanoaggregates can efficiently impede the chance of chain overlap by isolating active species, demonstrating an exponential function in the reduction of entanglement density. Over, this investigation can effectively control the exponential increase in entanglement caused by elevated temperatures, which is crucial for the synthesis of weakly entangled UHMWPE at high temperatures.
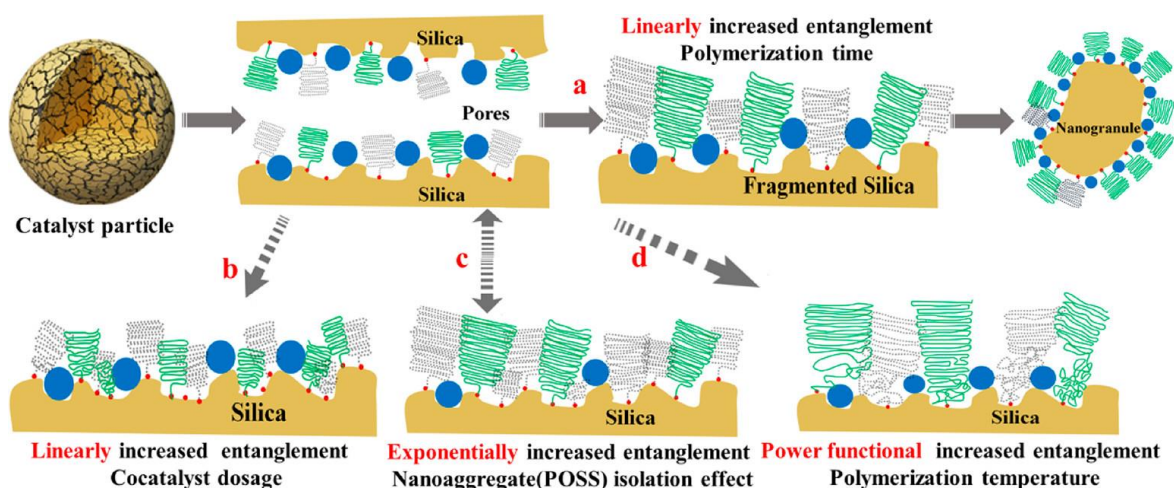

Figure 4. Schematic illustration of the entanglement formation mechanism of the nascent UHMWPE. Reprinted with permission from reference [40], copight American Chemical Society 2019.

To enable a facile synthesis of UHMWPE particles featured with several advantages in activity, processability, and mechanical properties, Chen et al. [41] have proposed a methodology for the preparation of ultrapure, weakly entangled UHMWPE with precise particle sizes by employing the POSS-modified $MgCl_2$-based Z-N catalyst. It was elucidated that POSS could effectively coordinate with the $MgCl_2(110)$ phase, serving as a cage structure embedded within the $MgCl_2$ support. This facilitated the uniform distribution of POSS nanosized particles, which in turn led to the confinement of active sites and enhanced the functionality of UHMWPE. The Cat-POSS-30% catalyst demonstrated a remarkable specific activity of 3.52×10^6 g PE·mol^{-1}[Ti]·h^{-1}·bar^{-1}, which was 3.2 times higher than that of Cat-POSS-0%. Such superior performance was attributed to the POSS-related nano-aggregates that prevented bimetallic deactivation. Similarly, a positive correlation was observed between specific activity and MW, with the highest achieved value of 142.5×10^4 g·mol^{-1} being obtained with Cat-POSS-30%. Furthermore, UHMWPE/POSS composites produced using Cat-POSS-10% and Cat-POSS-30% exhibited mean average particle size (D_{50}) values of 171 and 178 μm, respectively, indicating the production of submicron particles. In comparison to

Cat-POSS-0, Cat-POSS-10% and Cat-POSS-30% yielded UHMWPE with considerably smaller sizes due to increased activity. Notably, Cat-POSS-30% produced the most active catalyst based on $MgCl_2$, facilitating the production of weakly entangled UHMWPE. Interestingly, the initial storage modulus decreased with increasing activity, following a power function relationship (i.e., $G_N(0) = 2.77643 \times A^{-0.1575}$), suggesting a positive correlation between catalyst activity and enhanced impact strength. The incorporation of POSS from 0 to 30 wt% led to a significant 21.4% increase in impact strength, which was a result reduced entanglement density and refined particle size. Moreover, this study achieved an unprecedented impact strength of UHMWPE (113.6 kJ/m^2) despite its relatively lower molecular weight. Simultaneously, the tensile properties were also improved, with the tensile strength, Young's modulus, and break elongation increasing by 13.7%, 8.2%, and 11.2%, respectively. To investigate the effects of POSS on UHMWPE disentanglement, Zhou et al. [42] have incorporated soluble POSS (particularly, octaisobutyl-POSS) into UHMWPE using in-situ polymerization with [Al]/[Ti] ratio of 150 at 85 °C using triethylaluminum (TEA) cocatalyst. This method demonstrated several impacts, like reducing aggregation, augmenting the activation of the Z-N catalyst, and favorably affecting the MWD. The TEM investigation revealed a consistent distribution of POSS within the UHMWPE matrix, with particle size augmenting in proportion to the increase in POSS content. Meanwhile, the observed reduction in the rubbery plateau modulus indicated a downregulation in polymer entanglement. A decrease in viscosity suggested that POSS could facilitate molecular sliding and lubrication-driven expansion of entanglements, thus increasing the free volume. Further research indicated a reduction in M_e and entanglement density (V_e) of UHMWPE with low POSS concentration (0.05 to 0.2 wt%), clearly illustrating entanglement suppression. The low melt viscosities of the POSS/UHMWPE composites were associated with a POSS concentration of 0.2 wt%. Nevertheless, when the POSS content was elevated to 0.3 wt%, the viscosity escalated, attributable to the expanded diameters of the POSS domains. Notably, aggregation became significant at elevated levels of POSS ($\geq$ 0.3 wt%), resulting in a decrease in M_e and a rise in V_e. The results highlighted the influence of POSS domain size on polymer dynamics and the alignment of M_e and V_e trends with complex viscosity (η^*). Furthermore, estimates of melt activation energy indicated that the addition of POSS markedly diminished the annealing energy barrier of polymer chains, underscoring its essential function in the disentanglement of UHMWPE.

The production of UHMWPE with a fine particle size and few entanglements is still a major challenge for both industry and academia. To address this issue, Guo et al. [43] developed a novel hetero Z-N catalyst (4POSS-Cat) using 4-OH POSS and δ-$MgCl_2$ (yield, 93.1%) as the supporting framework. The catalyst exhibited irregular, block-shaped particles with diameters between 0.1 μm and 10 μm, containing POSS nanocrystals as active site insulators (**Figure 5**). Moreover, the POSS nanocrystal of 4POSS-Cat demonstrated remarkable chemical stability following Ti alterations. The highly reducible cocatalyst significantly enhances the catalytic efficacy of 4POSS-Cat, producing UHMWPE resins with a wider MWD that is still lower than that of C-UHMWPE resins. Subsequent analysis revealed that

the ideal Ti incorporation for 4POSS-Cat was 5.8%, exhibiting an activity of 6.052×10^6 g PE·mol^{-1}[Ti]·h^{-1}. Moreover, diminished Ti loading (namely, 1.0 and 3.1 wt%) resulted in decreased activity in ethylene polymerization, attributable to the rapid reactivity of TiCl$_4$ with POSS nanocrystals. The 4POSS-Cat catalyst exhibited considerable sensitivity to temperature fluctuations, and the entanglement of UHMWPE increased linearly with rising temperature due to imbalances in chain crystallization and propagation rates. All synthesized UHMWPE exhibited a low $G_N(0)$, signifying a reduced number of entanglements compared to C-UHMWPE. Conversely, the mean diameter of UHMWPE particles was under 120 μm, indicating small particle size attributes. As a result, tensile strength (39.4 MPa), Young's modulus (383.5 MPa), impact strength (102.7 kJ/m^2), and break elongation (940.5%) were enhanced by 11.1%, 13.7%, 24.6%, and 39.3%, respectively. The synthesized UHMWPE powder with 4POSS-Cat catalyst demonstrated significant reliability and the potential for performance assessments and pilot-scale trials.
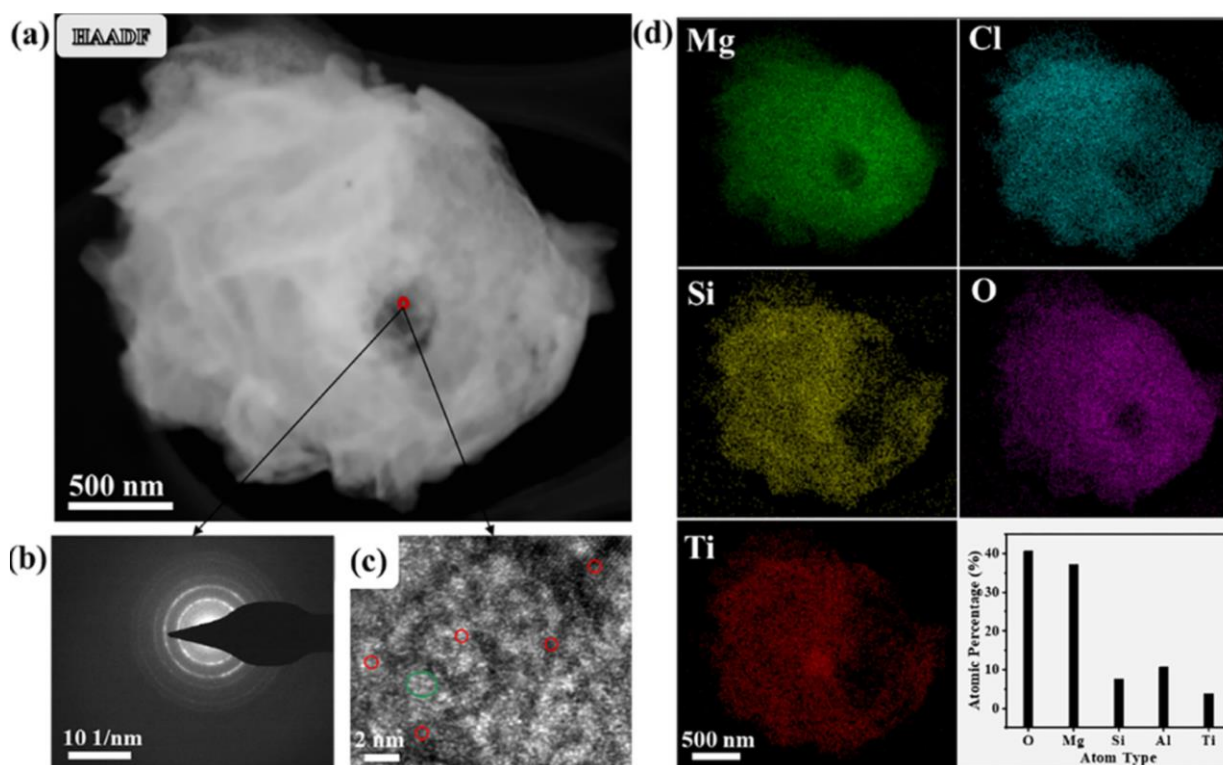

Figure 5. Characterization of the hetero Z-N catalyst (4POSS-Cat) using 4-OH POSS and δ-MgCl$_2$ as the supporting framework. Reprinted with permission from reference [43], copyright American Chemical Society 2022.

Notably, different dealcoholizing methods and the modification of active centers by POSS could also be performed to modify the distance between growing chains. Herein, Zhou et al. [44] have developed various novel Z-N catalysts with POSS by the utilization of various MgCl$_2$ dealcoholization techniques and OH-POSS modifications of active sites, which exhibited superior activity and thermal stability in ethylene polymerization at 85 °C and 65 °C (**Figure 6**). The products derived from all of these catalysts possess a MW up to 100×10^4 g/mol, thereby signifying the successful synthesis of UHMWPE and POSS/UHMWPE composites. The catalyst efficiency ranged from 7×10^6 g PE·mol^{-1}[Ti]·h^{-1} to 19×10^6 g PE·mol^{-1}[Ti]·h^{-1},

which endowed them with potential for industrial application. Moreover, studies on entanglement have demonstrated that an adequate space between the propagating chains is a predominant factor influencing the entanglement level of the synthesized UHMWPE. In-depth research has shown that physical dealcoholization has been shown to be more efficient in enhancing the catalyst specific surface area (SSA), leading to increased reactivity and improved catalytic performance among these methods. Herein, with the increase in SSA, the dispersion of active centers is enhanced, effectively precluding the sintering of each other. As a result, physically dealcoholized catalysts consistently lead to the production of UHMWPE with a lower level of entanglement. Notably, through systematic research, the authors have also discovered that if the POSS structure and its modified functional groups are inappropriate, they can have a negative impact on the disentanglement of the prepared UHMWPE molecular chains. This finding provides a significant reference for the design of POSS-based catalysts, enabling the avoidance of unnecessary detours in research and development.
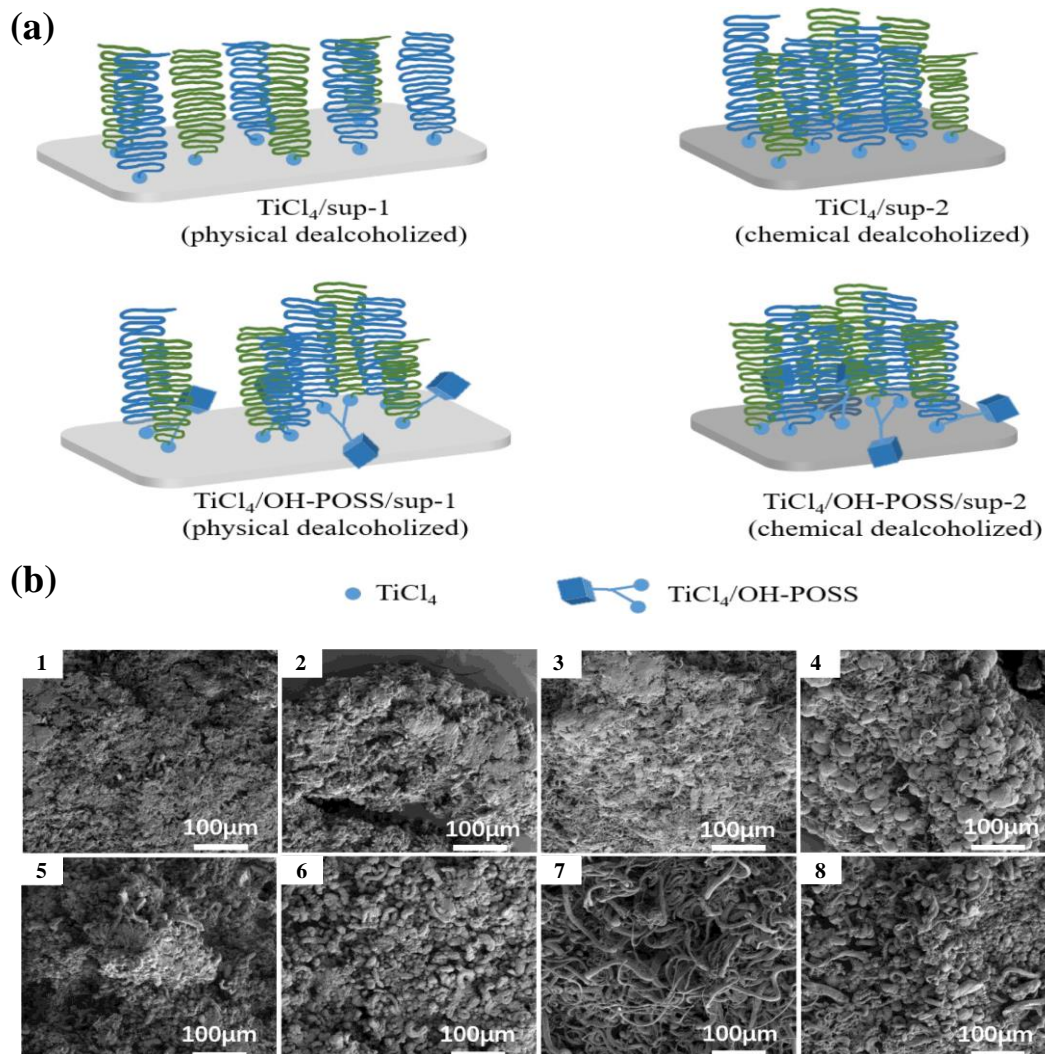

Figure 6. The disentanglement mechanism and product characterization of the dis-UHMWPE using different dealcoholization techniques. Reprinted with permission from reference [44], copyright American Chemical Society 2022.

3.2. Other modification methods based on Z-N catalyst

Considering that POSS were not able to diffuse into the pores with small size (less than 10 nm), Cao et al. [45] fabricated mildly entangled UHMWPE through a Z-N catalyst, in which $TiCl_4$ was immobilized onto polystyrene (PS)-functionalized silica. The ethylene polymerization process was carried out using a Büchi stainless steel autoclave reactor (1.0 L) equipped with a high-speed agitation device. The reactor was initially heated to 90 °C under vacuum for a minimum of 4 h, followed by nitrogen (N_2) purging three times. Subsequently, *n*-heptane (350 mL) was added to the reactor. A specific ratio of catalyst (SiO_2/X% PS/$TiCl_4$, 30 μmol) and TEA ([Al]/[Ti] = 100) were separately introduced into the reactor. The polymerization temperature was maintained at 70 °C, and the reaction was conducted at 10 bars of ethylene pressure and 500 rpm. The resulting dis-UHMWPE products were designated as PE-SiO_2/X%PS (X = 0, 2, 4, 6). In their ingenious design, the functionalized silica was prepared by in-situ radical polymerization of styrene, which was preloaded into the support pores. The embedded PS functioned as a barrier to partition the UHMWPE propagation chains, thereby alleviating entanglement even during extended polymerization periods at 70 °C. Notably, the enhanced effectiveness in reducing entanglements enabled the production of dis-UHMWPEs with significantly increased MWs upon prolonging the polymerization time. Consequently, the balance between toughness, stiffness, and strength of the produced UHMWPE was improved. Notably, a remarkable enhancement in impact resistance (114 kJ/m^2, +53.5%), Young's modulus (+80 MPa, +188.2%), tensile strength (31.4 MPa, +44.2%), and break elongation (696%, +16.6%) was observed in the UHMWPE synthesized using the catalyst SiO_2/6%PS.

Chammingkwan et al. [46] have developed an innovative approach utilizing a nano-dispersed MgO/$MgCl_2$/$TiCl_4$ core-shell catalyst for the production of UHMWPE with reduced entanglement. Polyoxyethylene alkylamine (PA) was employed to enhance the dispersion of MgO nanoparticles in a hydrocarbon solvent, ensuring the preservation of the primary particles. The polymerization was incrementally saturated with N_2 via a sequence of purging and evacuation cycles. Heptane served as the solvent, with TEA as the activator, and both were injected into the reactor before ethylene saturation under continuous agitation (70 °C, 0.8 MPa, for 30 min). Thereafter, a suitable dosage of the catalyst (10 mg–15 mg) was introduced to initiate polymerization. Following a 2-hour reaction time at 70 °C and 0.8 MPa, the resulting UHMWPE powder underwent vacuum drying at 60 °C for 6 hours. The lack of holes and the thorough dispersion of initial particles during polymerization facilitated fast crystal formation, preventing disruption from restricted polymer chains. The variable active site density of this catalyst, along with the choice of co-catalyst, enabled the synthesis of UHMWPE with reduced entanglement levels while maintaining appropriate activity levels. Furthermore, the annealing behavior, rheology, and solid-state drawability of the produced polymer confirmed the effectiveness of this method under industrial circumstances. Besides, the polymer's melting curve was studied via DSC, revealing a steep initial T_m that subsequently decreased during reheating. The solid-state processing of dis-UHMWPE was exemplified by knotting a 0.5 cm × 2 cm segment derived from a

compression-molded film fabricated at 140 °C and 20 MPa. The brief time of film compression (5 min) may prevent polymer chain tangling. Ink displacement indicated that dis-UHMWPE can be drawn at temperatures between 125 °C–130 °C up to 20 times. Conversely, C-UHMWPE demonstrated early failure at a low draw ratio owing to entanglement. The exceptional solid-state drawability of PE-0.5 highlighted its improved processability and validated its loosely entangled configuration.

Significantly, the initial entangled state and particle size play a crucial role in the sintering kinetics of UHMWPE. To enhance comprehension of solid-state sintering, Wang et al. [47] have fabricated nascent UHMWPE particles that possess comparable MWs but vary in terms of their initial entanglement states and diameters. The synthesis of UHMWPE with a lower degree of entanglement was carried out under a polymerization temperature of 50 °C and an ethylene pressure of 3 bar. To modulate the polymerization milieu, high-purity N_2 at 3 bar was incorporated into the slurry polymerization system, which effectively reduced the ethylene concentration in the proximity of the polymers. Consequently, the polymerization rate was markedly decreased to 2.4×10^6 g PE·mol^{-1}[Ti]·h^{-1}, and the formation of entanglements was inhibited. In contrast to conventionally synthesized UHMWPE (C-UHMWPE), highly entangled UHMWPE contains a multitude of physically intertwined points within highly entangled regions. These points significantly impede the mobility of chain segments, thereby restricting interfacial chain fusion and the progression of entanglement formation. Conversely, in the case of low entangled UHMWPE with heterogeneous dispersed entanglement, chain segment movement is facilitated. This promotes the formation of chain entanglements during the sintering process, especially the reconnection of entanglements at the interface region. This phenomenon offers a thermodynamic interpretation of the elimination of grain boundaries between the original particles, which augments the formation of entangled networks and co-crystallization at the interface of the cured particles (**Figure 7**). Furthermore, regardless of the entanglement level of UHMWPE, smaller particles possess a larger surface area available for bonding, which can stimulate chain diffusion and particle fusion. In the context of less entangled UHMWPE, the tensile strength and Young's modulus remain relatively stable and exhibit minimal dependence on particle size and sintering duration. This is attributable to the more rapid development of entanglements in less entangled UHMWPE. Overall, this outcome endorses the elimination of particle boundaries in sintering of UHMWPE materials, enhancing the fused particle networks and interfacial co-crystal density [55]. As a result, considerably shorter sintering times are adequate to achieve outstanding mechanical properties, which greatly highlights its enhanced melt processing capacity.
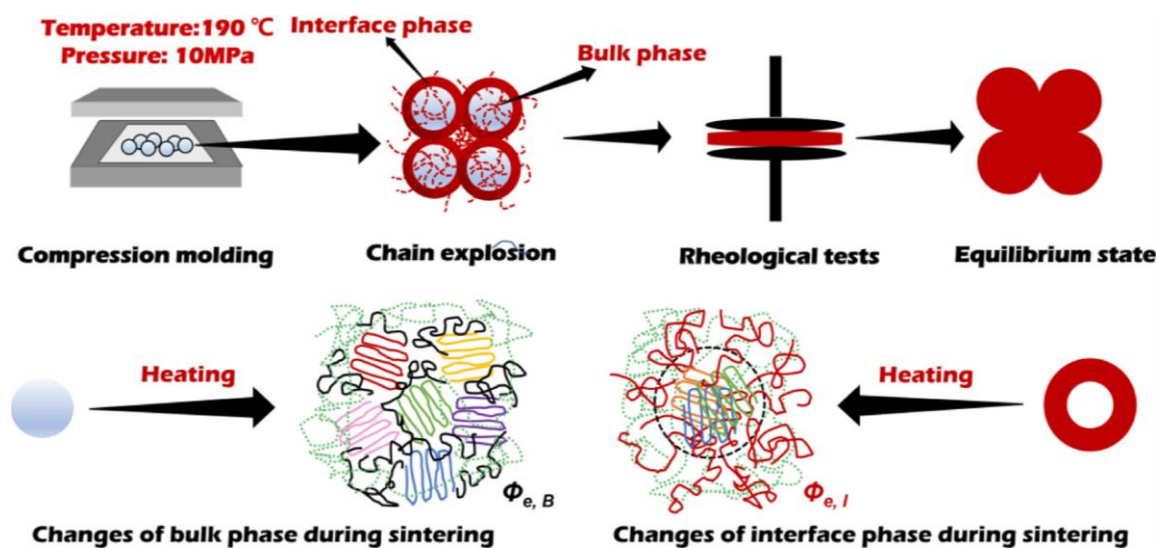
Figure 7. Schematic illustration of compression molding and rheological tests of synthesized dis-UHMWPE. Reprinted with permission from reference [47], copyright American Chemical Society 2022.

4. Conclusions

UHMWPE materials play a crucial role in economic and social development and are closely related to Z-N catalysts, which play an extremely crucial role in the industrial production of UHMWPE. This is primarily due to their remarkable catalytic efficacy, significant influence on the molecular weight of UHMWPE, and extensive applications in the industrial sector, all of which are highly prominent and evident. Nevertheless, UHMWPE synthesized using Z-N catalysts typically exhibits high degree of entanglement. Given that chain entanglement is of fundamental importance in modifying the processability and mechanical properties of nascent UHMWPE, the synthesis of dis-UHMWPE becomes essential for achieving industrial scalability and thus holds substantial practical significance. This review comprehensively summarizes the recent progress in optimizing Z-N catalysts for the synthesis of dis-UHMWPE. It provides a detailed and all-encompassing overview of research advancements, clearly elucidates polymerization conditions, establishes connections between polymer structure and catalytic activity, and introduces the design principles underlying polymerization techniques. We anticipate that this summary could provide valuable references and design inspiration for related researchers, thus facilitating the research field and performance potential of UHMWPE materials.

Conflict of interest: The authors declare no conflict of interest.

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