

Judicious Reduction of Supported Ti Catalyst Enables Access to Disentangled Ultrahigh Molecular Weight Polyethylene

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S Supporting Information

ABSTRACT: Heterogeneous Ziegler—Natta and homogeneous metallocene catalysts are known to produce ultrahigh molecular weight polyethylene (UHMWPE) in the entangled state. On the other hand, only (two) homogeneous single-site catalysts are reported to yield *disentangled* UHMWPE (*dis*-UHMWPE). This disparity between the two types of catalysts and the two states of polyethylene can be bridged if a heterogeneous single-site catalyst that can yield *dis*-UHMWPE is made accessible. Here, one-pot two-step synthesis of a MgCl₂ supported [Ti(OEt)₄] derived catalyst 1 with a two-stage activation strategy is reported to produce *dis*-UHMWPE.



Second activation of catalyst 1 was performed by adding excess modified methylaluminoxane (MMAO12), and XPS analysis indicated that the catalyst existed in only Ti(III) state at [AI]/[Ti] ratio of 600. Catalyst 1 after second activation with MMAO12 was found to be highly active in ethylene polymerization and produced *dis*-UHMWPE. Polymerization conditions were tailored to obtain molecular weight (M_w) as high as 13 million g/mol PE. To the best of our knowledge, this is the first time a heterogeneous catalyst (catalyst 1) that displays pseudosingle site nature is able to produce *dis*-UHMWPE. The thus-prepared nascent polyethylene revealed a melting temperature of 141–144 °C, which is a characteristic melting transition for a *dis*-UHMWPE. The disentangled state of the nascent PE and its M_w and MWD were further authenticated by rheological investigations. Isothermal time sweep oscillatory experiments in linear viscoelastic limit revealed a rapid rise in elastic modulus followed by equilibration to plateau modulus, which are characteristic features of the disentangled state. Thus, a pseudo-single-site heterogeneous catalyst has been accessed, which upon second activation with excess MMAO12 led to the production of *dis*-UHMWPE.

INTRODUCTION

Among the 300 odd million tons of polymers produced today, polyolefins constitute nearly half of the total volume and are most commonly manufactured by employing the supported Ziegler–Natta (ZN) catalyst.¹⁻⁶ The mode of action and fundamental principles of the Ziegler-Natta polymerization were deeply investigated in the early 1970s, and the monometallic mechanism proposed by Cossee-Arlman is unequivocally accepted by the scientific community.^{/-} Conventional ZN catalysts are known to be multisite in nature, as the alkylaluminum used for activating Ti(IV) precursor leads to titanium species with mixed oxidation states, which probably coexist in the catalytic system.¹⁰ Among other reasons, the existence of Ti in various oxidation states is believed to be responsible for regularly observed broader molecular weight distribution (MWD) in ZN-catalyzed olefin polymerization reaction.^{11–13} Therefore, detecting the distribution of oxidation states of a ZN catalyst and quantifying them has become indispensable, if we were to advance the seemingly matured olefin polymerization reaction. However, it is an impeding challenge to detect the distribution of oxidation states of titanium in a supported ZN catalyst and quantify them. This is

especially inconvenient due to the extreme air and moisture sensitivity of ZN catalysts, and such studies have been rarely undertaken. About a decade ago, Somorjai and co-workers took up this challenge and investigated the oxidation states of a model ZN catalyst using high-resolution X-ray photoelectron spectroscopy (XPS).¹⁴ Their investigation concluded that after reaction with triethylaluminum, the Ti species exists in Ti(IV), Ti(III), and Ti(II) states with different peak intensities. A consequence of simultaneous existence of multiple oxidation states is broadening of molecular weight distribution and a compromise on the properties offered by the polymer. Remarkably, their findings revealed that the predominant oxidation state of an activated titanium in the model catalyst was Ti²⁺, which contradicts the previous belief that the active species in a ZN system is generally a Ti³⁺ species.¹⁰ Although the above model system probably mimicked the actual catalytic system, access to a single site heterogeneous catalytic system in reality remains a formidable challenge. In contrast to the

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Figure 1. Representation of current state of the art in UHMWPE and dis-UHMWPE synthesis known in the literature.

multisite heterogeneous ZN catalytic systems, homogeneous catalytic systems such as metallocene yield a single-site catalyst that produces polyolefins with narrow MWD.^{15,16}

An edge the single-site catalysts (metallocene, postmetallocene, etc.) holds over the multisite ZN system is their ability to produce high to ultrahigh molecular weight polyethylene (UHMWPE).¹⁷⁻¹⁹ Among the homogeneous single-site catalytic systems, bis(phenoxy-imine)-based complexes of group IV metals (FI) are known to produce UHMWPE in a controlled manner and provide an unprecedented route to synthesize disentangled UHMWPE (dis-UHMWPE) (Figure 1).²⁰⁻²² Recently, Enders and co-workers^{23,24} reported a hemimetallocene-chromium catalyst capable of yielding UHMWPE, which was then tamed by Romano et al. to produce *dis*-UHMWPE.²⁵ The *dis*-UHMWPE is a speciality material as it offers the strongest commercially available films, easy to draw and easy to deform into oriented tapes with a high degree of chain alignment. Rastogi and co-workers have developed a polymerization process to produce *dis*-UHMWPE using single-site FI catalyst.^{26–33} Thus, an overview of literature reports depicted in Figure 1 suggested that it is only the singlesite homogeneous catalysts that are reported to produce disentangled ultrahigh molecular weight polyethylene.³⁴ In this context, a paradigm shift could be achieved if a heterogeneous single-site catalyst yielding dis-UHMWPE can be accessed. Although highly desirable, access to single-site heterogeneous catalytic system is almost unexplored and rarely reported.³⁵

Herein, we report controlled reduction of Ti(IV) precursor to Ti(III) species using suitable amount of modified methylaluminoxane (MMAO12). The resultant Ti(III) state yields a pseudo-single-site heterogeneous catalytic system which is capable of producing *dis*-UHMWPE. The existence and quantification of Ti(III) state has been demonstrated using X-ray photoelectron spectroscopy, and the disentangled state of the ultrahigh molecular weight polyethylene was unfolded by rheological investigations and thermal analysis.³⁸

RESULTS AND DISCUSSION

Synthesis of Catalyst 1 and Establishing the Oxidation States. Excess anhydrous magnesium chloride was treated with titanium(IV) ethoxide in hexane. Subsequently, the heterogeneous mixture was activated by adding excess amount of diethylaluminum chloride (DEAC). Anhydrous work-up followed by washing and drying yielded a blackish-brown powder of the anticipated catalyst (1). The solid-state (CP-MAS: cross-polarization magic angle spinning) proton NMR spectrum of this solid revealed a resonances at

0.77 and 3.88 ppm (Figure S1). These peaks could be assigned to the methyl (CH_3) and methylene (CH_2) groups present on the titanium, respectively. The proton NMR finding was further supported by ¹³C CP-MAS NMR which displayed peaks at 17.8 and 71.1–76.1 ppm (Figure S2) which can be assigned to methyl and methylene carbons, respectively.³⁹ The metal content of catalyst 1 was determined by inductively coupled plasma– optical emission spectroscopy, which revealed 3.02% Ti, 17.83% Mg, and 1.12% Al in the catalyst. Morphological characteristics of catalyst 1 were obtained using scanning electron microscopic (SEM) analysis. The SEM image of catalyst 1 is displayed in Figure 2. The SEM image clearly shows that the particles are spherical or oval in shape with an average size of 109–206 nm.



Figure 2. SEM image of the catalyst 1.

After having established the characteristics of 1, second activation was carried out by treating 1 with MMAO12, and the change in oxidation states of titanium was recorded by X-ray photoelectron spectroscopy (XPS). Ti 2p XPS spectra collected from catalyst 1 before and after the addition of MMAO12 are shown in Figure 3. Two distinct peaks corresponding to the spin—orbit split of 2p centered around 458 and 464 eV are discernible from the Ti 2p core-level spectrum. The XPS of the Ti $2p_{3/2}$ peak for the Ti(OEt)₄/MgCl₂ system activated with diethylaluminum chloride was deconvoluted with titanium species in 4+, 3+, and 2+ oxidation states. The binding energy values are in line with the reported values.⁴⁰ Quantification of different Ti oxidation states shows the following composition: 25.7% of Ti(IV) [BE = 459.7 eV], 56.8% of Ti(III) [BE = 457.2



Figure 3. Ti 2p XPS spectra of catalyst 1 before addition of MMAO12 (top), after addition of MMAO12 [AI]/[Ti] = 20 (center), and after addition of MMAO12 [AI]/[Ti] = 600 (bottom).

eV], and 17.5% of Ti(II) [BE = 454.4 eV]. The reason for the presence of multiple oxidation states of surface Ti species could be because of the reduction of Ti^{4+} [Ti(OEt)₄] in the presence of organoaluminum in an uncontrolled manner, resulting in a multisite catalyst toward olefin polymerization. The activation with MMAO12, for [Al]/[Ti] ratio = 20, revealed minor changes in Ti oxidation states where all the Ti species were

shifted to slightly higher binding energy side by approximately 0.5 eV with Ti center existing in 4+, 3+, and 2+ oxidation state likewise. This is expected as addition of MMAO12 can lead to reduction of titanium precursor. However, after addition of MMAO12 at [AI]/[Ti] ratio = 600, the Ti⁴⁺ and Ti²⁺ peak intensities decreased drastically, and we could only fit one type of Ti species, i.e., Ti³⁺ [BE = 457.7 eV]. Thus, the catalyst with [AI]/[Ti] ratio = 600 gave a strong indication to be a pseudo-single-site catalyst with Ti³⁺ as the only detectable oxidation state. The oxidation state distribution on the surface of the Ti catalyst was obtained from Ti 2p XPS peaks of the titanium species before (addition of MMAO12) and after addition of MMAO12 with [AI]/[Ti] ratio 20 and 600, respectively. The Ti 2p XPS peaks for these samples are shown in Figure 3, and a quantitative distribution of Ti valence states is listed in Table 1.

Table 1. XPS Data of the Catalyst 1 at the Ti 2p_{3/2} Level

no.		$Ti \ 2p_{3/2}$	peak BE (eV)	atomic %
1	before addition of MMAO12	Ti ⁴⁺	459.7	25.7
		Ti ³⁺	457.2	56.8
		Ti ²⁺	454.4	17.5
2	MMAO12 $[Al/Ti] = 20$	Ti ⁴⁺	460.2	22.2
		Ti ³⁺	457.7	70.8
		Ti ²⁺	454.8	7
3	MMAO12 $[Al/Ti] = 600$	Ti ⁴⁺		
		Ti ³⁺	457.7	>99
		Ti ²⁺		

Disentangled Ultrahigh Molecular Weight Polyethylene (dis-UHMWPE). Some of the supported Ziegler-Natta type catalysts are known to produce high to ultrahigh molecular weight polyethylenes. Magnesium chloride supported titanium tetrachloride activated with triisobutylaluminum is reported to produce a maximum viscosity-average molecular weight of 7.8 million g/mol at 60 °C and 7 bar of ethylene pressure after 2 h. Along the same lines, when triethylaluminum is used as cocatalyst, a maximum weight-average molecular weight of 4.2 million g/mol is obtained at 40 °C and 1 bar ethylene pressure in 2 h.41 Similarly, TiCl₃ activated with diethylaluminum chloride yielded 6 million g/mol (at 65 °C, monomer pressure of 5.5 bar after 1 h). While, a higher molecular weight of 10.5 million g/mol was obtained when the same catalyst was supported on MgCl₂, and the polymerization was performed at 40 °C and at a very high ethylene pressure of 20.7 bar for 1 h.42 When an equimolar mixture of triisobutylaluminum and isoprenylaluminum was used to activate a MgCl₂ supported TiCl₄ catalyst, a molecular weight of 10–15 million g/mol was obtained (at 75 °C, ethylene pressure of 7.6 bar) after 2 h.⁴³ In most of the above reports, there were no data about the polydispersity and there was no evidence for entangled or disentangled state of the resultant UHMWPE. Given the conditions applied for polymerization, it is reasonable to assume that the above catalysts produced entangled UHMWPE with a broad molecular weight distribution.44 In one recent report, the metal-organic framework was utilized to build a single-site heterogeneous catalyst composed of Ti(III)-, Ti(IV)-, and Cr(III)-MFU-4l (MFU-4l = $Zn_5Cl_4(BTDD)_{34}$ $H_2BTDD = bis(1H-1,2,3-triazolo[4,5-b],[4',5'-i])dibenzo-1,4$ dioxin).45 The thus-prepared catalyst was activated in the presence of cocatalyst MAO or triethylaluminum to produce PE with a M_w of 1.4 million g/mol (PDI = 2.3 at 9 bar of ethylene pressure). However, the state (entangled or

run	Al/Ti	time (min)	temp (°C)	yield ^b (g)	activity ^c (kg _{PE} /mol Ti/h/atm)	$M_{\rm w}^{d}$ (10 ⁶ g/mol)	PDI ^d	$T_{\rm m}^{\ e}$ (°C)	cryst ^f (%)
1	without MMAO12	10	40	no polymer					
2	without 1	10	40	no polymer					
3	20	10	40	no polymer					
4	100	10	40	0.05	24	1.08	1.93		
5	400	10	40	0.83	398	1.23	1.86	142.8	54.5
6	600	10	40	1.4	671	2.07	1.84	142.2	67.44
7	800	10	40	1.35	647	1.01	2.00	142.1	66.1
8	1000	10	40	1.34	642	1.09	2.25	142.1	65.1
9	600	10	0	0.20	96	3.29	1.73	142.5	82.4
10	600	10	20	0.48	230	2.11	1.75	142.3	72.3
11	600	10	60	3.21	1538	1.35	2.10	141.3	70.2
12	600	30	40	3.75	600	3.05	1.83	142.6	70
13	600	60	40	5.5	440	7.03	1.87	143.0	46.1
14	600	90	40	5.2	277	10.89	2.04	142.8	64.6
15	600	120	40	5.32	213	13.07	2.17	144.1	69.7
16 ^g	600	10	40	1.56	374	3.32	2.24	142.4	75.7
17 ^h	600	10	40	1.60	153	3.91	2.25	142.6	68.1
18	600	60	0	0.47	38	9.48	1.89	142.9	84

Table 2. Polymerization of Ethylene Catalyzed by Supported Ti Catalyst 1 in the Presence of MMAO12^a

^{*a*}Conditions: catalyst = 12.5 μ mol of Ti (20 mg of catalyst); solvent = 150 mL of toluene. ^{*b*}Obtained from gram of polyethylene isolated. ^{*c*}Activity = kg of PE/[mol of Ti]/atm/h]. ^{*d*}As obtained from HT-GPC at 160 °C in 1,2,4-trichlorobenzene (TCB) against polystyrene standards, in 10⁶ g/mol. ^{*e*}Obtained from DSC, first heating cycle. ^{*f*}Crystallinity calculated from the melting enthalpy measured by DSC and relative to the theoretical value for 100% crystalline polyethylene. ^{*b*}S bar ethylene pressure.

disentangled) of the resultant UHMWPE remains unexplained. $^{\rm 45}$

After having established access to titanium catalyst 1 with a predominant Ti³⁺ oxidation state, we set out to examine the performance of this catalyst in ethylene polymerization. The polymerization reactions were carried out in Büchi highpressure reactor in the presence of MMAO12 as a second stage activator, and the important polymerization results are summarized in Table 2. The most influential polymerization parameters, such as metal to MMAO12 ratio, temperature, ethylene pressure, and time, were screened to obtain maximum molecular weight and narrow molecular weight distribution. After polymerization, the polymer molar mass $(M_w \text{ and } M_n)$ and molar mass distribution (MWD) was determined using high-temperature gel permeation chromatography (HT-GPC) at 160 °C in 1,2,4-trichlorobenzene (Figures S7-S12). The identity of the resultant polyethylene was established using high-temperature proton and carbon NMR spectra. A clean single resonance in the proton NMR was observed at 1.23 ppm (Figure S5) which can be ascribed to the methylene protons of polyethylene. The high-temperature ¹³C NMR spectrum revealed a single peak at 30.4 ppm (Figure S6), which can be easily assigned to the repeating methylene carbon. Observation of a single carbon resonance suggests that there are almost no methyl branches, which is indicative of low or no β -hydride elimination. The absence of methyl branches suggests the existence of highly linear polyethylene.^{46,47} As is evident from Table 2, polymerization could not take place in the absence of modified methylaluminoxane (MMAO12) or catalyst 1 (Table 2, runs 1 and 2). In homogeneous metallocene or postmetallocene catalyzed polymerization of olefins, methylaluminoxane (MAO) or modified MAO (MMAO12) is commonly used in large (Al:M = 1000-20000) excess.^{48,49} Therefore, the effect of [Al]/[Ti] ratio on the activity and molecular weight of polyethylene was evaluated first. Initial polymerization with [Al]/[Ti] ratio of 10 or 20 was largely unsuccessful (Table 2, run 3). However, at a [Al]/[Ti] ratio of

100, a few milligrams of polyethylene was obtained. It was found that the activity increases with increasing [Al]/[Ti] ratio from 100 to 600 (Table 2, runs 4–6) (activity = 671 kg_{PE}/mol Ti/h/atm). However, there was a drop in activity to 642 kg_{PF} mol Ti/h/atm when the [Al]/[Ti] ratio was further increased to 800 or 1000 (Table 2, runs 7 and 8). A similar trend was observed for weight-average molecular weight (M_w) , and the highest $M_{\rm w}$ of 2.07 \times 10⁶ g/mol was observed at a [Al]/[Ti] ratio of 600. The decrease in M_w upon increasing MMAO12 above the limit of 600 can be explained by chain transfer to trimethylaluminum (TMA). The trimethylaluminum is usually present in MMAO12, and with increasing concentration of MMAO12, the amount of TMA increases leading to increase in chain transfer and subsequent reduction in molecular weight. Please note that the polydispersity index for these runs (run 4-8) remained close to 2, which indicates a pseudo-single-site nature of this supported catalyst.⁵⁰⁻⁵³

One of the compelling parameters that influence the degree of entanglement, molecular weight, and activity is the polymerization temperature. In order to suppress entanglement during polymerization, the rate of chain propagation should be lower than the rate of crystallization. This can be achieved by performing polymerization at low temperature. However, the rate of polymerization decreases with lowering polymerization temperature. Therefore, for the successful synthesis of disentangled ultrahigh molecular weight polyethylene, one has to strike a right balance between the rate of polymerization and rate of crystallization (disentanglement) of polyethylene. In our attempts to strike this balance and identify suitable temperature, the polymerization reactions were performed between 0 and 60 °C at the [Al]/[Ti] ratio 600 at ambient ethylene pressure in toluene for 10 min. The highest M_w of 3.3×10^6 g/ mol (Table 2, run 9) was observed at 0 $^{\circ}$ C, while increasing the temperature to 60 °C led to reduced molecular weight of 1.35 \times 10⁶ g/mol (Table 2, run 11). The low molecular weight at high temperature could be due to enhanced β -hydride elimination or chain transfer reactions at 60 °C. Although the

highest molecular weight was observed at 0 $^{\circ}$ C, but the activity observed was the lowest (Table 2, run 9) under these conditions. The optimal balance between activity, molecular weight and temperature was stricken at 40 $^{\circ}$ C (Table 2, run 6).

The above two parameters, [AI]/[Ti] and temperature, were kept constant, and the effect of time on polymer molecular weight and catalytic activity was investigated. As it is apparent from runs 6 and 12-15 (Table 2) and Figure 4, the molecular



Figure 4. Plots of M_n and M_w/M_n (PDI) as a function of polymerization time for ethylene polymerization at [Al]/[Ti] ratio 600, 1 bar of ethylene pressure, and 40 °C in toluene.

weight linearly increases with increasing time. The effect of time was investigated from 10 to 120 min, and the results indicate that the catalyst displays living behavior, as the molecular weight keeps increasing with time. After 120 min, the molecular weight builds up to a whopping 13 million (13.07 \times 10^6) g/mol with narrow molecular weight distribution (PDI = 1.84–2.17). These observations indicate pseudo-single-site nature and living behavior of the catalytic system.⁵⁴ Next, the effect of ethylene pressure was investigated, and the polymerization reactions were conducted at 1, 2, and 5 bar of ethylene pressure under identical conditions ([Al]/[Ti] = 600; 40 °C; toluene = 150 mL, time = 10 min.). As expected, molecular weight increases with increasing ethylene pressure, and a maximum $M_{\rm w}$ of 3.91 \times 10⁶ g/mol was obtained at 5 bar ethylene pressure (Table 2, run 17) (Figure S12). This observation can be attributed to the increasing concentration of ethylene at higher ethylene pressure, leading to abundant availability of the monomer for polymerization. However, catalytic activity decreases significantly as a result of slow diffusion of ethylene through the fast growing polymer chain.²⁶

The performance of the supported catalyst 1 prepared in this investigation is compared with known supported as well as homogeneous catalysts in Table 3. As it is evident from Table 3, the supported ZN catalyst activated with triethylaluminum (TEAL) displays an activity of 8.1 kg_{PE}/mol Ti/h/atm with a $M_{\rm w}$ of 2.1 \times 10⁶ g/mol and a PDI of 4.4 (Table 3, run 1).⁵⁵ Under identical conditions, catalyst 1 revealed a much higher activity of 213 kg_{PE}/mol Ti/h/atm with a $M_{\rm w}$ of 13.07 \times 10⁶ g/ mol and a PDI of 2.17 (Table 3, run 2).⁵⁶ The activity, higher molecular weight, and narrow PDI suggest that MMAO12 is a better activator than the traditional TEAL. One of the most active homogeneous catalysts in the area of disentangled UHMWPE is pentafluorophenoxyimine derived titanium catalyst (FI).^{57,58} Unfortunately we could not come across any literature report on ethylene polymerization using FI catalyst under identical conditions, but run 3 in Table 3 summarizes the closest conditions to our investigations (Table 3, run 4). Note that in this reported experiment MAO was used as cocatalyst instead MMAO12 used in this study, and almost double the amount of MAO (Al:Ti = 1100) was employed.⁵⁹ The FI catalyst displayed the highest activity of 4910 kg_{pe}/mol Ti/h/atm with a $M_{\rm w}$ of 5.2 \times 10⁶ g/mol and a PDI of 3.1 (Table 3, run 3). While under identical conditions (except the cocatalyst), catalyst 1 was found to be 8 times less reactive and displayed lower molecular weight (Table 3, run 4). Enders and co-workers recently reported chromium based homogeneous catalyst that is capable of producing UHMWPE.²³ The authors reported that naphthyridine cyclopentadienyl chromium catalyst yields UHMWPE with an activity of 8.67 kgpe/mol Cr/h/atm with a $M_{\rm w}$ of 0.48 \times 10⁶ g/mol and a PDI of 2.5 (Table 3, run 5).⁶¹ In this polymerization, pMAO was used as cocatalyst at a [A1]: [Cr] = 1000. Under identical conditions, catalyst 1 revealed a much higher activity (153 kg_{PE}/mol Ti/h/ atm), $M_{\rm w}$ (3.91 × 10⁶ g/mol), and similar PDI (~2) (Table 3, run 6). Thus, the heterogeneous catalyst 1 developed in this investigation displayed lower activity then the state-of-the-art homogeneous FI catalyst but was found to be highly active compared to the standard heterogeneous ZN catalyst and homogeneous Cr catalyst.

Thermal and Melt Behavior of the Polyethylene. The melting and crystallization temperature was obtained from differential scanning calorimetry data (Figures S13–S19). The first melting peak (T_{m1}) obtained from the first heating cycle was in the range 141.3–144.1 °C for the polyethylenes prepared in this investigation, whereas, the second melting peak (T_{m2}) obtained from the second heating cycle varied between 134.6 and 135.7 °C. Thus, in general, second melting peaks were approximately 7–8 °C lower than the first melting peaks. This behavior is indicative of disentangled state of UHMWPE.

Table 3. Comparison of Activity, Molecular Weight, and Molecular Weight Distribution^a

run	cat.	temp (°C)	time (min)	ethylene (bar)	$activity^{c}$ (kg _{PE} /mol Ti/h/atm)	$M_{\rm w} \ (10^6 \ { m g/mol})$	PDI (GPC)	ref
1	het ZN	40	120	1	8.1	2.1	4.4	55
2	cat. 1	40	120	1	213	13.07	2.1	60
3	FI ^b	40	30	1	4910	5.2	3.1	59
4	cat. 1	40	30	1	600	3.05	1.83	60
5	Cr cat. ^c	40	10	5	8.67	0.48	2.5	61
6	cat. 1	40	10	5	153	3.91	2.25	60

^{*a*}Conditions: for detailed polymerization conditions, please go through the cited reference. ^{*b*}Note that this experiment was performed using MAO instead of MMAO12, and almost double the amount of MAO (Al:Ti = 1100) was used. ^{*c*}Note that this experiment was performed using pMAO instead of MMAO12, and almost double the amount of pMAO (Al:Cr = 1000) was used.



Figure 5. DSC plots of the *dis*-UHMWPE sample (Table 1, run 13) obtained from the second heating cycle (Fig. 8 ramp G-H) with annealing time of 5, 15, 30, and 60 min.



Figure 6. Time sweep data of PE4 sample for about 48 h. The equilibrium storage modulus is attained after about 37 h. The G' value increases from 0.96 to 1.82 MPa over the course of that time.

The first melting peak of the nascent PE is attributed to formation of single crystal lamellae, which is a hallmark of the disentangled state, whereas the peak after second melting indicates the hindrance to formation of single crystal lamellae due to presence of entanglements formed after first heating.^{26,38,62} The degree of crystallinity of the majority of the nascent PE samples was above 60%, as analyzed from

enthalpy of the first melting peak relative to the theoretical melting enthalpy of 293 J/g for 100% crystalline PE.⁶³ The maximum crystallinity of 82% and 84% was obtained for a polymerization run at 0 °C for 10 min and 1 h (Table 1, runs 9 and 18), respectively.

To further investigate the disentangled state of the polyethylene obtained using catalyst 1, DSC experiments



Figure 7. Dynamic frequency sweep of the PE samples after the equilibration in the time sweep. G' and G'' are represented by solid lines and dashed lines, respectively (top). The modulus crossovers of PE1 and PE2 are indicated by red circles. The data for PE2 are shown separately at the bottom for clarity.

were performed using a thermal analysis protocol developed by Rastogi and co-workers.³⁸ At a time when the semicrystalline polymer is molten, the disentangled polymer chains in the noncrystalline phase tend to entangle, leading to a heterogeneous distribution of entanglement density in melt.³⁸ The difference in heterogeneity in the entanglement density of the disentangled samples was generated using a reported protocol, where the nascent PE sample was heated from 50 °C to an annealing temperature of 160 °C at the heating rate of 10 °C/ min and then annealed for different time intervals, i.e., 5, 15, 30, and 60 min. After annealing, the sample was cooled to an isothermal crystallization temperature of 128 °C where it was allowed to undergo isothermal crystallization for 180 min. Subsequently, the sample was cooled to 50 °C before the second heating from 50 to 160 °C. The DSC curves obtained from the second heating cycle after annealing for 5, 15, 30, and

60 min are plotted Figure 5. The presence of dis-entangled PE was confirmed by the appearance of two separate melting peaks in DSC curve, after annealing and isothermal crystallization for stipulated time. A lower temperature melting peak at 134 °C and a higher temperature melting peak at 139.5 °C indicate the crystallization from entangled and disentangled domains of the heterogeneous polymer melt, respectively.³⁸ Furthermore, it was found that the ratio of area under the low and high melting temperature peaks changes with the annealing time (at 160 °C). Thus, the ratio of area under higher temperature melting peak decreases and eventually the area under lower temperature melting peak (entanglement density) increases with increasing annealing time from 5 to 60 min. This phenomenon is in line with the previous report and is associated with the transformation of the heterogeneous distribution of entanglement density to homogeneous state.³⁸

Small-Amplitude Oscillatory Rheology. Figure 6 shows results of isothermal time sweep oscillatory test for a representative sample run 18 from Table 2. The storage modulus is seen to increase with time and eventually saturates after about 48 h. The rise in G' is rapid initially followed by more gradual increase until saturation. These trends are indications of the disentangled state of the sample, in agreement with the DSC results. The disentangled state is intrinsically metastable and has lower elasticity. During isothermal annealing, the chains reorganize to achieve the equilibrium entangled state, which has higher elasticity. Hence, G' increases as seen in Figure 6. All samples showed similar time sweep behavior indicating that they were synthesized in disentangled states. Small-amplitude frequency sweep measurements were then performed on four samples, viz. runs 7, 6, 13, and 18 from Table 2, which were labeled as PE1, PE2, PE3, and PE4, respectively, at 190 °C. According to HT-GPC, the molecular weights of these UHMWPE samples are ordered as PE1 < PE2 < PE3 < PE4.

Frequency sweeps were performed only after the equilibrium entangled state of the samples was attained, i.e., after approximately 48 h in a time sweep at 190 °C. The storage moduli (G') and viscous moduli (G'') of the samples are plotted in Figure 7 (top). Additionally, the G', G", and tan δ of the sample PE2 are displayed separately in Figure 7 (bottom). The storage moduli increase with increase in molecular weight. For the lower molecular weight samples, crossovers of the storage (G') and viscous (G'') moduli curves are seen at (0.01)rad/s, 0.105 MPa) for PE1 and at $(4 \times 10^{-3} \text{ rad/s}, 0.131 \text{ MPa})$ for PE2. No crossovers are seen in PE3 and PE4 due to the high molecular weights of the samples. As shown in Figure 7 (bottom) for PE2, the G' shows a weak but finite frequency dependence after crossover frequency, and the G'' data show a peak at frequencies higher than the crossover frequency. These are indications of some amount of polydispersity in the samples.⁶⁴ Similar behavior was seen for all the other three samples. Following Talebi et al.²⁸ and using the in-built software of ARES G2 (Trios), the molecular weight distributions of the samples were calculated from the rheological response. The PE samples were assumed to have unimodal log-normal distribution, which is the usual case for PE synthesized with Ziegler-Natta catalysts.⁶⁵ The relaxation time exponent x in the relation $\lambda \sim (M_w)^x$ was fixed in the range 3.3-3.6, with the higher values being used for lower molecular weight samples and lower values for higher molecular weight samples. This is in line with theoretical understanding that reptation will be the dominant relaxation mechanism for the higher molar mass PE,⁶⁶ while additional mechanisms such as constraint release will also contribute to stress relaxation for the lower molar mass PE.⁶⁷ The plateau modulus was estimated using $G_{\rm N}^0 \approx \rho RT/M_e^{.68}$ Here ρ is the melt density of PE, the temperature T = 190 °C, and R is the universal gas constant. The entanglement molecular weight M_e was taken to be 1250 g/mol, which is a reasonable assumption for UHMWPE at 190 ^oC.⁶⁴

The molecular weights of the sample calculated from this method are given in Table 4. These are seen to be in close agreement with the experimentally measured values using HT-GPC. However, the polydispersity indices calculated from rheological methodology were higher than the results reported by HT-GPC. The absolute weight-average molecular weight in HT-GPC was measured using a light scattering (LS) detector. However, measurement of PDI requires both LS and RI

Table 4. Comparison of the HT-GPC Results and MWD Calculated from Rheology for the Selected Disentangled UHMWPE Samples

	HT-GPC r	esults	rheological MWD results			
UHMWPE sample	M _w (×10 ⁶ g/mol)	PDI	M _w (×10 ⁶ g/mol)	PDI	$ \stackrel{``x" in \lambda}{(M_w)^x} \sim $	
PE1	1.00	2.00	1.04	3.72	3.6	
PE2	2.07	1.84	2.07	4.14	3.5	
PE3	7.03	1.87	7.04	9.78	3.4	
PE4	9.48	1.89	9.64	7.78	3.33	

detectors. Since GPC measurements were done using very dilute samples, there may be some errors in determination of concentration by the RI detector. Thus, a plausible reason for the difference in PDI values obtained from rheology and GPC may be attributed to the errors in RI detector measurements.

Higher PDIs can be expected for UHMWPEs reported in the present work relative to those reported for UHMWPEs synthesized by FI catalysts because of two possible reasons: (a) Catalyst concentrations used in the polymerization step reported here are much higher than those typically used in polymerization by single-site FI type catalysts. Thus, growing chains are likely to encounter each other and will tend to entangle in the present case than in the cases reported in the literature. (b) There could be small amounts of other Ti species with different oxidation states which are below the detectable range of XPS. The heterogeneity in the active species could lead to greater polydispersity. Nevertheless, the rheology data would be more reliable for such high molecular weight polyethylene.

CONCLUSIONS

In summary, treatment of magnesium chloride with titanium-(IV) ethoxide and first activation by diethyl aluminum chloride yields catalyst 1 as a blackish-brown solid. The identity of catalyst 1 was unambiguously ascertained by a combination of spectroscopic and analytical methods. Thus, solid-state (CP-MAS) proton and carbon NMR spectra of 1 revealed the appearance of methyl and methylene protons at 0.77 and 3.88 ppm, respectively, and the corresponding carbons at 17.8 and 71-76 ppm. ICP-OES analysis disclosed about 3.01% loading of titanium on the magnesium chloride support. In our attempts to access, identify, and quantify the oxidation states, catalyst 1 was doubly activated with a variable amount of MMAO12, and the oxidation states of the resulting catalysts were accessed by X-ray photoelectron spectroscopy. As evident from Table 1, treatment of catalyst 1 with [Al]/[Ti] ratio of 600 led to quantitative reduction of Ti(IV) to Ti(III). A characteristic Ti 2p_{3/2} peak for Ti³⁺ was observed at a binding energy of 457.7 eV, which is in line with the reported value.⁴ After having established access to a supported catalyst with predominant Ti³⁺ state, the performance of 1 was evaluated in ethylene polymerization. Catalyst 1 after second activation with MMAO12 was found to be highly active in ethylene polymerization and produced very high molecular weight polyethylene. The effect of MMAO12 on molecular weight, molecular weight distribution, and activity was investigated, and a [Al]/[Ti] ratio of 600 produced the optimal balance between $M_{\rm w}$, MWD, and productivity. Thus, at [Al]/[Ti] = 600, PE with a weight-average molecular weight of 2.07×10^6 g/mol and an activity of 671 kg_{PE}/mol Ti/h/atm was obtained. The highest $M_{\rm w}$ with minimum activity was observed at 0 °C, whereas



Figure 8. Thermal analysis protocol.

minimum $M_{\rm w}$ and maximum activity were evidenced at an elevated temperature of 60 °C. Remarkably, catalyst 1 displayed a living behavior over the period of 2 h and a maximum $M_{\rm w}$ of 13.07 × 10⁶ g/mol with a narrow MWD was attained. Comparison of literature known heterogeneous catalyst and state-of-the-art homogeneous catalysts suggests that the hitherto unknown catalyst 1 after second stage activation with MMAO12 outperforms its heterogeneous counterpart and chromium-derived homogeneous system but falls short of the FI catalyst. Nevertheless, to the best of our knowledge, this is the first time a heterogeneous catalyst (catalyst 1) that displays pseudo-single-site behavior is able to produce disentangled ultrahigh molecular weight polyethylene.

The thermal properties of the resultant dis-UHMWPE were investigated using DSC. In the first heating cycle, the nascent polyethylenes revealed thermal transition at around 141-144 °C, which is a characteristic melting transition for a disentangled UHMWPE. The DSC investigations demonstrated that the entangled state (melting at around 134 °C) and disentangled states (melting at around 140 °C) coexist in the second heating cycle. Similar observations have been reported by Rastogi and co-workers under identical thermal program. Thus, from the DSC investigations it is apparent that the nascent polymer obtained is in the disentangled state. The disentangled state of the PE, molecular weight, and molecular weight distribution were further corroborated by rheological investigations. Isothermal time sweep experiments showed that the elastic modulus increased with time reaching plateau values after about 48 h. This corroborates the DSC evidence of disentangled nature of the as-synthesized PE. The rheologically determined molar mass agreed well with the absolute weightaverage molecular weight obtained from light scattering detector of HT-GPC. Rheological measurements suggest higher polydispersity in molar mass distribution than that expected for a truly single site catalyzed polymer. However, this could be due to the higher catalyst concentration used during polymer synthesis. Thus, a pseudo-single-site heterogeneous catalyst has been developed in a one-pot process, which upon second activation with MMAO12 led to the production of disentangled ultrahigh molecular weight polyethylene.

EXPERIMENTAL SECTION

Materials. Unless noted otherwise, all manipulations for air- and moisture-sensitive compounds were performed under an argon

atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. Titanium(IV) ethoxide, toluene, and hexane were purchased from Spectrochem Pvt. Ltd., Mumbai, India. Titanium(IV) ethoxide was used as received, and toluene/hexane was dried over sodium/ benzophenone in an argon atmosphere and freshly distilled prior to use. Ethylene (99.995%; 4.5 grade) was supplied by Ms. Vadilal Chemicals Ltd., Pune, India. Diethylaluminum chloride (DEAC) was obtained from Crompton GmbH. Anhydrous magnesium chloride and modified methylaluminoxane (MMAO-12, 7 wt % aluminum in toluene) were obtained from Sigma-Aldrich and used as received. Antioxidant Irganox 1010 was purchased from Ciba.

XPS Analysis. XPS measurements were carried out using Thermo Scientific K-alpha+ X-ray photoelectron spectrometer (XPS). As the catalyst is air/moisture sensitive, a specially designed vacuum transfer module was used to transfer samples from a glovebox environment into the K-Alpha⁺ system without exposure to air. The details of the vacuum transfer module and complete sample preparation are described in Supporting Information.

NMR Measurements. All solid-state NMR spectra were recorded on a Joel 400 spectrometer, resonating at 100 MHz for ¹³C and 400 MHz for ¹H, using a 4 mm double resonance MAS probe. High-temperature NMR of the UHMWPE sample was recorded at 130 °C in C₆D₆ + TCB (10:90) on a 500 MHz machine (Bruker Avance).

Determination of Molar Mass (M_w) and Molar Mass Distribution (PDI). Weight-average molecular weight (M_w) , number-average molecular weight (M_n) , and polydispersity index (PDI) of the synthesized disentangled UHMWPEs were recorded in 1,2,4-trichlorobenzene at 160 °C by a Viscotek GPC (HT-GPC module 350A) instrument equipped with the triple detector system. The detectors were calibrated with linear polystyrene standards, and the reported molecular weights are absolute molecular weights.

Scanning Electron Micrographs. The morphology of the catalyst 1 was investigated using a high-resolution FEI QUANTA 200 3D Environmental SEM. The sample was suspended in hexane and placed on silicon wafer. The samples were coated with gold by a sputtering technique.

Thermal Analysis. A TA Instruments Q-10 or Q-100 differential scanning calorimeter (DSC) was utilized to obtain the melting temperatures (T_m) and subsequent melt enthalpies. To minimize the thermal lag caused by the samples, the weight is kept within 6 ± 0.1 mg for each sample. During the measurement, nitrogen was continuously purged at 50 mL/min. A thermal protocol has been devised to obtain samples having different entanglement densities by following a literature reported method as depicted in Figure 8.³⁸ The sample was heated from 50 °C to an annealing temperature which is higher than PE's equilibrium temperature (145 °C) at 10 °C/min to 160 °C. At this temperature, the sample was annealed for a fixed time (5, 15, 30, and 60 min.). Four different annealing times were chosen to vary entanglement density in melt. Next, the sample was cooled to an

isothermal crystallization temperature of 128 $^{\circ}$ C at a 10 $^{\circ}$ C/min rate. The sample was kept on hold at isothermal crystallization temperature for a fixed time of 180 min. Next, the sample was cooled to 50 $^{\circ}$ C, and second heating was done from 50 to 160 $^{\circ}$ C at 10 $^{\circ}$ C/min. The DSC plots shown in Figure 5 were obtained during this second heating ramp.

Rheology Measurements. The melt properties of the polyethylene were measured using an 8 mm aluminum parallel plate geometry on a strain-controlled rheometer (ARES G2). The PE samples (along with 0.7 wt % antioxidant Irganox 1010) were compacted into an 8 mm diameter disc of 1 mm thickness at room temperature using a hand-held mold. The disc was loaded into the rheometer at 110 °C. The temperature was increased to 130 °C at a heating rate of 30 °C/min while a constant axial force of 1 N was applied on the sample. The temperature was then ramped up to 190 $^{\circ}C$ at a rate of 10 $^{\circ}C$ /min while the axial force was stepped up to 4 N. This method of heating and application of axial load is adapted from the literature⁵⁹ and is done to avoid slippage and ensure adequate contact between the sample and the rheometer plate. Once the temperature of the sample reached 190 °C, a time sweep was performed at a frequency of 10 rad/s with a strain of 0.5% for about 48 h, after which a dynamic frequency sweep was performed on the sample at 190 °C. The frequencies tested were from 600 to 6×10^{-4} rad/s at a strain of 0.5%.

Elemental Analysis. To know the weight percent of Ti, Al, and Mg in synthesized heterogeneous catalyst 1, elemental analysis was performed on an inductively coupled plasma optical emission spectrophotometer (ICP-OES) [model: SPECTRO ARCOS Germany, FHS 12 instrument].

Synthesis of Catalyst 1. In a three-neck round-bottom flask equipped with a magnetic bar, nitrogen inlet, and a condenser, 40 mL of freshly distilled dry *n*-hexane was added followed by 0.5 g (2.19 mmol) of titanium(IV) ethoxide and 3 g (31.51 mmol) of anhydrous magnesium chloride. The reaction mixture was refluxed for an hour with constant stirring. Subsequently, the temperature of the reaction mixture was brought to room temperature, and 3.184 g (3.31 mL) of diethylaluminum chloride (DEAC) in 10 mL of dry *n*-hexane was added dropwise over a period of 20 min, and the reaction mixture was refluxed for 2 h. The thus-obtained blackish slurry was cooled to room temperature and washed with three portions of freshly distilled dry *n*-hexane (3 × 25 mL). Finally, the solid catalyst 1 (yield: 3.46 g) was dried under vacuum and stored in glovebox for further usage.

¹H CP-MAS NMR (400 MHz, 298 K): δ = 3.88 (broad, s, CH₂), 0.77 (broad, s, CH₃). ¹³C CP-MAS NMR (100 MHz, 298 K): δ = 76.1–71.1 (m, OCH₂, Ti(OEt)₄), 32.3 (m, CH₂, *n*-hexane), 25.7 (m, CH₂, *n*-hexane), 17.8 (m, CH₃, Ti(OEt)₄), 8.2 (m, CH₂, DEAC), 1.6 (s, CH₃, DEAC).

Elemental Analysis. Analysis was done using ICP-OES. Following is the catalyst composition observed: Ti 3.01%; Al 1.12%; Mg: 17.83%.

Synthesis of MMAO-12-Treated Catalyst. In a round-bottom Schlenk flask, 50 mg (0.031 25 mmol) of catalyst 1 and 7.25 mL (18.75 mmol, 600 equiv) of MMAO-12 were added, and the mixture was stirred for about an hour at room temperature. Subsequently, the reaction mixture was washed with three portions of freshly distilled dry *n*-hexane (3×10 mL each). Finally, the solid product was dried under vacuum and stored in a glovebox for further analysis.

General Procedure for Ethylene Polymerization. The polymerization was run in a Büchi glasuster cyclone 075 high-pressure reactor equipped with an overhead mechanical stirrer, heating/cooling jacket, and pressure regulators. A predried 250 mL Büchi reactor was kept under vacuum at 95 °C for 1 h before usage. After cooling down, the reactor was filled with argon, and after three cycles of vacuum/ argon, the reactor was filled with ethylene gas. It was charged with 130 mL of freshly distilled toluene at room temperature under the positive flow of ethylene gas. The reaction temperature was set to the desired value using Julabo temperature controller, and after the thermal equilibrium is reached, 70% of total amount of MMAO-12 was added and the mixture was stirred for about 30 min. Simultaneously, in a separate Schlenk tube, 20 mL of freshly distilled toluene was taken, and the remaining amount of MMAO-12 (30%) was added and the

content was stirred for 30 min (to quench air and moisture from toluene if any). After 30 min, a suitable amount of catalyst was injected into the reactor along with 20 mL of dry toluene containing MMAO12, and the polymerization was initiated by pressuring the reactor with ethylene. The polymerization was carried out for the required time under vigorous stirring and constant feed of ethylene and then terminated by addition of acidified methanol. The polymer was filtered out, washed with a copious amount of methanol/acetone, and dried overnight under vacuum at 60 °C to obtain free-flowing powder. The polymerization results have been summarized in Table 2.

¹H NMR (500 MHz, [C₆D₆ + TCB (10:90),] 130 °C): δ = 1.23 (broad, s, CH₂). ¹³C NMR (125 MHz, [C₆D₆ + TCB (10:90),] 130 °C): δ = 30.4 (s, CH₂).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b00590.

Detailed characterization of catalyst **1**, polymerization, and melt properties of the resultant disentangled ultrahigh molecular weight polyethylene, complete characterization of *dis*-UHMWPE, spectroscopic and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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