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Note

Catalysts for UHMWPE and UHMWPE-copolymers

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ABSTRACT

Classic inorganic and more recent organometallic compounds capable of polymerizing ethylene to ultra high molecular are compared. Activated catalysts showed varying degrees of productivity when challenged with co-monomers. The general activity trend followed $TiCl_3 < Mg/Si–TiCl_3 <$ metallocenes. A new phenoxyimine catalyst complex *N*-(3,5-diiodosalicylidene)cycloheptylamine titanium dichloride was useful in making UHMWPE and compared to previously reported phenoxyimine catalyst structures capable of living polyolefin polymerizations.

1. Introduction

Ultra high molecular weight polyethylene (UHMW-PE) is one of the toughest plastics known, with very high abrasion resistance and low coefficient of friction. Gear parts are machined from UHMW-PE, gel spun fibers are woven into bullet proof vests, bearings are machined into components for artificial joints. Preferred more than metal on metal, ceramic on ceramic or a combination thereof, UHMW-PE has distinct advantages when used in arthroplastic applications [1], and it has been the material of choice as hip, knee, and shoulder components, balancing biological compatibility and durability [2].

Joint components made from UHMW-PE may last for a decade or more without incident, but as with most moving parts, failure is inevitable: wear via micronization and fractures are two of the major mechanisms. Many studies providing improvements in processing and the way in which UHMW-PE is handled and formed which have produced positive results [3]. However, with the exception of cross-linking, fundamental changes in the macromolecular structure related to polymer improvements have not been described: studies on comonomer incorporation into UHMW-PE have also been limited [4–7].

Polyolefin catalysts come in a wide variety; they have been commercially developed over many years for unique performance characteristics and tailored for specific applications [8]. The activated catalytic reaction center plays a crucial role in tailoring the macromolecular chain sequence. Classic titanium trichloride Ziegler–Natta (Z/N) catalysts and current generation magnesium and silica supported titanium chloride catalysts, with many different active sites, produce broadly molecular weight distributed polymers and (in the case of co-polymers) have co-monomer distributed in the low molecular weight fractions [9]. Single site catalysts such as metallocenes and "new century" catalysts produce polymers having a narrow distribution and have random comonomer chemical distributions [10]. Each system has advantages in tailoring macromolecular properties.

In a series of reports describing UHMW-PE polymers and copolymers made using a variety of polyolefin catalysts, we reported our initial studies [4,5]. This contribution elaborates on catalyst activities and comonomer incorporation with the various classes and we present synthesis and polymerization results on a novel single site phenoxyimine complex designed for making UHMW-PE polymers.

2. Experimental

2.1. Catalysts and synthetic methods

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise indicated. Classic $TiCl_3$ Ziegler–Natta catalysts used in these studies were made following literature methods [11]. A commercially available magnesium chloride/silica supported Ziegler–Natta

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Catalysts: W.R. Grace Sylopol® 5917 was used for comparison. Metallocene catalysts were purchased from Boulder Scientific (Boulder CO), or Aldrich; supporting methods have been reviewed [12] and protocols applied as previously reported [5]. The phenoxy-imine catalysts used in these studies were synthesized using standard methods described in the literature [13,14] with some modification (described below).

2.2. Synthesis of FI catalysts

2.2.1. N-(3,5-Diiodo-salicylidene)-2,6-difluoroaniline

3,5-Diiodo-salicylaldehyde (10 g, 27 mmol) and 2,6-difluoroaniline (3.5 g, 27 mmol) were added to a 50 mL round bottom flask affixed with a toluene filled Dean-Stark trap and condenser fitted with a N_2 adapter. Toluene (100 mL) was added to the flask and the solution was heated to reflux and stirred overnight. The solution is concentrated to ~25 mL and heptanes (~150 mL) are added with stirring to precipitate the product as an orange solid. The solid was collected by filtration, dried under vacuum and used to make the complexes. The solid was characterized by GC/MS which had one peak with a *m/z* 485. ^{1}H NMR ($CDHCl_2$): $\delta = 14.1$ (s, 1H), $\delta = 8.7$ (s, 1H), $\delta = 8.1$ (s, 1H), $\delta = 7.6$ (s, 1H), $\delta = 7.3$ (s, 1H), $\delta = 7.0$ (m, 2H).

2.2.2. Ti, Zr, Hf metal complexes

N-(3,5-Diiodo-salicylidene)-2,6-difluoroaniline (4.85 g, 0.01 mol) and THF were added to a Schlenk flask under N_2. The solution was cooled to −78 °C and 2.5 M *n*-BuLi (0.01 mol) was added dropwise through a septum. The cooling bath was removed and the yellow solution becomes orange as it was allowed to come to room temperature. The solution was stirred for 2 h and then cooled again to −78 °C. MCl_4 (0.005 mol); (M = Ti, Zr, Hf) was added to the solution. The cooling bath was removed and the solution was stirred overnight. The solution was pumped dry *in vacuo* and the remaining solid was dissolved in CH_2Cl_2. This solution was filtered through Celite with the filtrate pumped dry in vacuo. Pentanes were added and the slurry was stirred rapidly for 2 h. The solid was allowed to settle and the solution decanted off. The solid was pumped dry leaving a powder as product (Ti: red, Zr: yellow/orange, Hf: yellow). Yield ranged from 40% to 60%. ^{1}H NMR for Ti complex (isomers: spectral shifts were similar for Zr and Hf complex; $CDHCl_2$): $\delta = 8.7$ (s, 2H), $\delta = 8.2$ (m, 2H), $\delta = 7.7$ (m, 2H), $\delta = 7.1$ (m, 6H).

2.2.3. N-(3,5-Diiodo-salicylidene)cycloheptylamine (see Fig. 1)

3,5-Diiodo-salicylaldehyde (37.3 g, 100 mmol) and cycloheptylamine (11.3 mL, 100 mmol) were added to a 1 L round bottom flask. Pentanes (300 mL) and molecular sieves were added. The solution was stirred at room temperature for 4 h and then filtered. The yellow solid was dissolved in pentane and the resulting slurry was filtered. The filtrates were combined and concentrated on the rotovap leaving the product as a bright yellow solid that was further dried in vacuo. The solid was characterized by GC/MS which had one peak with a *m/z* = 469; ^{1}H NMR ($CDHCl_2$): $\delta = 15.3$ (s, 1H), $\delta = 8.25$ (s, 1H), $\delta = 7.9$ (s, 1H), $\delta = 7.75$ (d, 1H), $\delta = 3.9$–3.3 (m, 1H), $\delta = 2.5$–1.2, (m, 12H).

2.2.4. Ti and Zr metal complexes

N-(3,5-Diiodo-salicylidene)cycloheptylamine (10 g, 21 mmol) and THF (100 mL) were added to a Schlenk flask under N_2. The solution was cooled to −78 °C and 2.5 M *n*-BuLi (9 mL, 22.5 mmol) was added dropwise through a septum. The cooling bath was removed and the yellow solution became orange as it was allowed to come to room temperature. The solution was stirred for 2 h and then cooled again to −78 °C. MCl_4 (21 mmol, M = Ti, Zr) was added to the solution. The cooling bath was removed and the solution was stirred overnight. The solution was pumped dry in vacuo and the remaining solid was dissolved in CH_2Cl_2 (50 mL). This solution was filtered through Celite and the filtrate pumped dry in vacuo. Pentanes (50 mL) were added and the slurry was stirred rapidly for 2 h. The solid was allowed to settle and the solution decanted off. This solid was pumped dry leaving a powder as product (Ti: red, Zr: yellow/orange). Yield = 60–65%; Typical ^{1}H NMR (Ti complex, isomers): δ (ppm) ($CDHCl_2$): 9.06 (s, 2H), 9.3–9.1 (m, 2H), 8.5–7.7 (m, 2H), 4.5–3.2 (m, 12H), 2.5–1.0 (m, 20H).

2.2.5. Hf metal complex

N-(3,5-Diiodo-salicylidene)cycloheptylamine (10 g, 21 mmol) and THF (100 mL) were added to a Schlenk flask under N_2. The solution was cooled to −78 °C and 2.5 M *n*-BuLi (9.0 mL, 22.5 mmol) was added dropwise through a septum. The cooling bath was removed and the yellow solution becomes orange as it was allowed to come to room temperature. The solution was stirred for 2 h and then the THF was removed in vacuo. Anhydrous toluene (50 mL) was then added to the flask which was cooled to −78 °C. $HfCl_4$ (6.7 g) was added to the solution. The cooling bath was removed and the solution was stirred overnight. The solution was pumped dry in vacuo and the remaining solid was dissolved in CH_2Cl_2 (50 mL). This solution was filtered through Celite and the filtrate pumped dry in vacuo. Pentane (50 mL) was added and the slurry was stirred rapidly for 2 h. The solid was allowed to settle and the solution decanted off. This solid was pumped dry leaving the product as a yellow powder. Yield = 70 %. Typical ^{1}H NMR (isomers): δ (ppm) ($CDHCl_2$): 8.06 (s, 2H), 8.03 (d, 2H), 7.5 (d, 2H), 3.8–3.3 (m, 12H), 2.2–1.2 (m, 20H).

2.3. Polymerization methods and conditions

Polymerization protocols were similar to those previously described [4]. Polymerizations were carried out in a jacketed 4 L stainless steel stirred tank reactor, 2.5 L of heptane or hexane was used as the solvent; 0.7 mmol triethyl aluminum (TEAl) was used as a scavenger. Depending on the system, catalysts were activated with diethylaluminum chloride (DEAC), triisobutyl aluminum (TiBAl), or methylalumoxane (MAO) at the levels indicated in the tables. Temperature was thermostatically controlled as indicated; pressure remained constant during the campaign (at levels indicated) with continuous monomer feeding. Co-monomers used in these studies were purchased from Aldrich or Boulder Scientific and used without further purification. In all cases co-monomers were charged to the reactor during initial loading of the reactor (prior to catalyst loading): no additional co-monomer was added during the polymerization campaign.

In a typical campaign, the reactor was heated to above 90 °C and purged with nitrogen for a minimum of 30 min prior to cooling under positive nitrogen pressure. Solvent (heptane) was added followed by co-monomer (hexene) and scavenger. The temperature was set at the desired set-point then polymerization grade ethylene gas was added to run pressure. Catalyst and activator solution (prepared in a nitrogen dry box) were injected using a pressurized stainless steel syringe pump or from a cylinder using nitrogen pressure.

Molecular weight of the polymers was calculated from the intrinsic viscosity (ASTM D4020); comonomer composition was measured using FTIR (see ASTM D5576, D6248 and references therein). ^{13}C-MAS-NMR was carried out by Acorn NMR Inc. (Livermore, CA).

3. Results and discussion

3.1. Classic Ziegler–Natta catalyst: polymerization results

We compared the activities of the various catalyst systems using identical polymerization conditions and at similar catalyst metal loadings. For the early Ziegler–Natta catalyst made by the straight-forward reduction of titanium tetrachloride using aluminum alkyls (in our example diethylaluminum chloride (DEAC) was used), polyethylene having a molecular weight well over 2 million Daltons can be achieved at commercially relevant temperatures (see Table 1). Typical for polyolefin catalysts, lowering the temperature or increasing the monomer concentration (pressure) of the polymerization increases the molecular weight of the polymer. The polymer molecular weight does not increase with time: this catalyst system is not living.

Addition of hydrogen to the $TiCl_3$ catalyst system can more than double the activity. Hydrogen is an effective chain transfer/polymer chain release agent. As the concentration of hydrogen is increased from 2.1 to 8.5 mmol in the reactor there is a decrease in polymer molecular weight from 4.3 MM down to 2.5 MM and a corresponding increase in mileage (see Table 2).

The effect on catalyst activity by the addition of co-monomers is also pronounced with this catalyst system. Adding small amounts of propylene to the catalyst system produces a dramatic reduction in activity and equally dramatic lowering of the molecular weight (see Table 3). The mol% of comonomer found in the polymer (as measured by FTIR), increases with increasing co-monomer fed to the reactor. Under our polymerization conditions molecular weights remain above 1 million Daltons even with increasing co-monomer content.

3.2. Supported $TiCl_3$ catalysts

In the generations following the classic self supported β- or γ-$TiCl_3$, supported catalysts were developed which were more active and required less downstream processing after polymerization [15]. These catalysts have surface active titanium and are used commercially to make a wide variety of homo and copolymer products. In most commercial cases, hydrogen is added to control molecular weight of the polymer product. We have taken one of the more recently developed commercially available catalysts designed for polyethylene polymerizations and run in the absence of hydrogen, thereby producing extremely high molecular weight polymer. In Table 4, polymerization results using Sylopol® 5917 in the absence of hydrogen produced polymers which were above 10 million Daltons. Some of these polymers were insoluble in testing solution under normal intrinsic viscosity measuring conditions.

As seen in Table 4, control over the molecular weight of the polymerization product is readily accomplished using temperature or pressure. The activity of this catalyst is affected by polymerization conditions (the catalyst is much more active at the higher temperatures and pressures), and can be more than ten times higher than that of the previous $TiCl_3$ version while maintaining more than adequate molecular weight.

Addition of increasing amounts of hexene co-monomer decreased the catalyst activity. However, molecular weight remained ultrahigh (see Table 5). Alternative co-monomers such as allylamine and decadiene were tested to provide functionality, also provided ultrahigh molecular weight polymers at the expense of catalyst activity.

Table 1
Results from ethylene polymerizations using $TiCl_3$.[a]

Cat. (mmol Ti)	Temp. (°C)	Press. (psi)	Time (min)	Polymer (g)	Acitivity (kg PE/mmol Ti/h)	IV (dL/g)	Mw × 10^{-6} (g/mol)
0.3	60	100	45	187	0.83	18.6	4.2
0.3	60	100	60	252	0.84	21.6	5.3
0.3	60	100	120	470	0.78	21.6	5.6

[a] Polymerization conditions: 4 L reactor, 45 mg catalyst, 1.6 mmol DEAC (activator).

Table 2
Effect of hydrogen on ethylene polymerizations using $TiCl_3$.[a]

Cat. (mmol Ti)	H_2 (mmol)	Temp. (°C)	Press. (psi)	Time (min)	Polymer (g)	Activity (kg PE/mmol Ti/h)	IV (dL/g)	Mw × 10^{-6} (g/mol)
0.2	2.1	65	100	120	630	1.56	18.9	4.3
0.2	4.4	65	100	90	480	1.60	14.6	2.9
0.13	8.5	65	100	60	275	2.12	12.3	2.3
0.12	8.5	65	100	30	170	2.83	12.7	2.4

[a] Polymerization conditions: 4 L reactor, 1.6 mmol DEAC (activator).

Table 3
Copolymer results at 60 °C, 2.5 L hexane with $TiCl_3$.

Cat amt (mmol)	Co-monomer	[M]	Time (h)	Press. (psi)	Yield (g)	Activity (kg PE/mmol Ti/h)	Mole (%)[a]	IV (dl/g)	Mw[b] × 10^{-3} (g/mol)
0.44	None	–	4.0	100	435	0.25	–	2.5	5058
0.44	Propylene	0.18	4.5	100	350	0.17	5.8	2.3	4521
0.44	Propylene	0.88	4.0	200	400	0.23	9.0	1.8	3387
0.44	Propylene	1.23	5.0	110	290	0.13	13.0	1.4	2388
0.44	1-Hexene	0.30	5.0	100	345	0.16	6.0	1.4	3624
0.44	1-Hexene	0.48	6.0	120	315	0.12	7.0	1.8	1680
0.44	1-Hexene/5-MHD[c]	0.30 0.19	3.5	100	427	0.28	3.5	1.2	1954

[a] Co-monomer content in polymer measured by ^{13}C-MAS NMR.

[b] Calc. from viscosity.

[c] 5-Methylhexadiene.

Table 4
Homo-polymerization results with Mg/Si supported Ti (Sylopol® 5917).[a]

Cat. (mmol Ti)	Temp. (°C)	Press. (psi)	Time (min)	Yield (g)	Activity (kg PE/mmol Ti/h)	IV (dl/g)	Mw[b] × 10^{-6} (g/mol)
0.005	30	80	60	3.0	0.6	27.4	7.39
0.008	30	100	30	3.5	0.9	20.0	4.66
0.008	30	100	180	37.0	1.5	33.7	10.12
0.008	30	200	60	12.0	1.4	33.1	9.86
0.009	30	200	180	126.5	4.9	Not soluble	
0.005	40	300	60	30.0	5.5	32.8	9.72
0.008	40	300	60	27.0	3.3	34.5	1050
0.010	45	150	120	130.0	6.8	Not soluble	
0.010	45	150	120	132.0	6.9	Not soluble	
0.009	45	150	120	106.0	6.0	Not soluble	
0.010	45	150	120	119.0	6.1	Not soluble	
0.008	60	100	180	235.0	9.4	26.5	7.10
0.009	60	100	60	27.0	3.0	24.9	6.50
0.008	60	200	60	300.0	36.8	23.1	5.78
0.009	60	200	120	298.7	17.4	27.9	7.64
0.008	60	200	180	597.0	24.0	25.1	6.55
0.016	60	300	30	250.0	32.3	23.0	5.75
0.008	60	300	60	185.0	22.7	25.9	6.84
0.009	80	80	60	298.8	34.3	15.2	3.11
0.010	85	100	180	525.0	18.4	18.2	4.10

[a] Polymerization conditions: 4 L reactor.
[b] Calc. from viscosity.

Table 5
Co-polymerization results with Mg/Si supported Ti (Sylopol® 5917).[a]

Cat. (mmol Ti)	Co-monomer[b]	Amt [M]	Temp. (°C)	Press. (psi)	Time (min)	Yield (g)	Activity (kg PE/mmol Ti/h)	IV (dl/g)	Mw × 10^{-6} (g/mol)
0.010	Hexene	0.08	60	200	180	518.0	18.1	27.0	7.30
0.010	Hexene	0.16	60	200	180	420.0	14.7	23.1	5.78
0.008	Hexene	0.32	60	40	240	154.0	4.7	27.6	7.2
0.016	Allyl amine	0.02	65	30	300	40.0	0.5	30.0	6.62
0.009	Decadiene	0.09	80	80	90	98.0	7.3	Not soluble	
0.014	Decadiene	0.11	25	200	60	10.0	0.7	Not soluble	

[a] Polymerization conditions: 4 L reactor, scavenger: TiBAl, 6.25 mmol; NS = not soluble.
[b] 1-Hexene, 1,9-decadiene.

3.3. Single site catalysts: metallocenes

Several metallocene catalysts were tested for making high molecular weight polyethylene: one of the more successful candidates at producing UHMWPE was the unbridged metallocene, bis-ethylcyclopentadienyl hafnium dichloride. Although incorporation of co-monomers such as hexene was realized, there was a drop in molecular weight using this catalyst system with hexene incorporation. The activity of these catalyst systems was also quite low as expected from hafnocenes activated with commercial MAO (see Table 6).

3.4. Phenoxy-imine (FI type) single site candidates

In our initial polymerizations using the FI catalysts (see Fig. 2), it was determined that the molecular weight under our polymerization conditions using catalyst (**1**) were higher than desired. In addition, the results from catalyst (**2**), although also in the range of the values reported in the literature, were less than required. For this reason, a marriage of the ligand components was used to produce the daughter complex (**3**), in anticipation of moderating molecular weight. Polymerizations were done using the previously described phenoxy-imine titanium catalysts (**1**) and (**2**) and the one catalyst structure previously unreported (**3**), which combined the ligand substitutions from the 2 reported structures.

As part of the controlled polymerization study, we re-examined the effectiveness of the di-fluorine-di-iodine containing phenoxy-imine catalyst (**1**): the homo-polymerization results from selected runs are presented in Table 7. For either of the ligand structures tested, the zirconium and hafnium complexes had little or no polymerization activities under the conditions used for testing the titanium complexes.

In all cases for complex (**1**), extremely high molecular weight polymers were produced. Lower molecular weight ranges could be achieved by lowering the polymerization temperature and increasing polymerization pressure, with polymer molecular weights in excess of 10 million g/mol. The living nature of the catalyst was also confirmed by increasing molecular weights with

Table 6
Ethylene copolymerizations with hexene using $(EtCp)_2HfCl_2$ (unsupported).[a]

Amt (mmol Hf)	1-Hexene Amt (ml)	Temp. (°C)	Press. (psi)	Time (min)	Yield (g)	Activity [kg PE/mmol Hf/h)	IV (dl/g)	Mw (g/mol) × 10^{-3}	FTIR (%)
0.027	–	45	100	60	108	4.0	12.0	2191	–
0.027	–	45	100	120	158	3.0	10.5	1790	–
0.027	0.16	44	100	60	120	2.2	6.5	881	1.50
0.027	0.64	42	100	120	219	4.0	3.2	297	4.75

[a] Polymerization conditions: 4 L reactor, Al/Hf = 1000, scavenger: TiBAl.

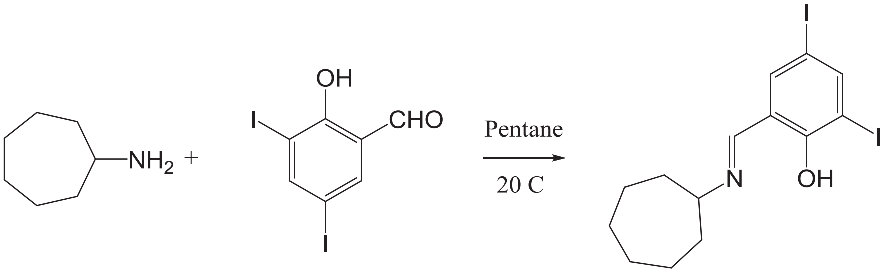
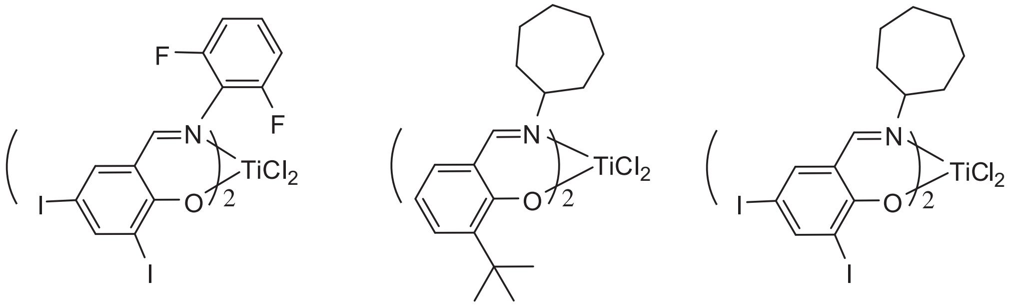


Fig. 1. Synthetic scheme for *N-(*3,5-diiodo-salicylidene)cycloheptylamine ligand. (a) 17287: See text for explanation of results.



(1) (2) (3)

Fig. 2. New Century (FI type) catalysts used in polymerizations.

Table 7
Homo-polymerizations with (**1**): $FI(F_2I_2)TiCl_2$.[a]

Lot	Cat (μmol)	Al/Ti	Temp (°C)	Press. (psi)	Run time (min)	Polymer (g)	(kg Pol/mmol cat/h)	IV (dl/g)	Mw[b] × 10^6 (g/mol)
17 248	4	2151	25	40	10	6.0	8.2	35.7	11
17 250	4	2151	25	40	40	11.0	3.7	40.0	13
17 282	5	2000	40	40	20	10.0	6.5	33.3	10
17 201	7	3691	45	300	60	67.1	9.4	28.4	7.8
17 014	6	1249	50	100	45	12.0	2.9	28.2	7.8
17 088	39	892	50	200	60	133.0	3.4	39.9	13
17 199	7	2060	55	300	60	18.1	2.5	33.4	10
17 190	3	2061	60	100	60	15.3	4.7	31.8	9.3
17 188	4	2061	60	300	45	45.0	14.0	41.6	13.9

[a] Polymerization conditions: 4 L reactor, 2.5 L heptane (solvent).
[b] Calculated from IV.

Table 8
Polymerizations with (**1**): $FI(F_2I_2)TiCl_2$ using 1-hexene as co-monomer.[a]

Lot	Cat. amt (μmol)	Ratio cat/cocat	Press. (psi)	Polymer (g)	(kg Pol/mmol cat/h)	IV (dl/g)	Mw[b] × 10^6 (g/mol)
17 236	7.4	2060	100	40.0	5.4	33.7	10.1
17 238	7.4	2060	100	41.5	5.6	36.9	11.6
17 242	6.2	2062	100	44.0	7.2	38.5	12.3
17 243	6.2	2062	100	41.0	6.7	35.0	10.7
17 245	6.4	1818	100	52.0	8.1	38.1	12.2
17 229	7.4	2060	250	43.2	5.9	38.1	12.2
17 228	4.6	2065	300	31.8	6.9	43.3	14.7

[a] Polymerization conditions: 2.5 L heptane (solvent), 25 ml 1-hexene (co-monomer); 45 °C polymerization temperature, 60 min. run time.
[b] Calculated from IV.

increasing polymerization time, although chain transfer to aluminum is effective at reducing this outcome.

In order to determine if there was a reduction in molecular weight by addition of co-monomer such a hexene, a number of polymerizations at varying conditions were performed (Table 8). At 0.08 M concentration of 1-hexene in heptane and varying temperature and pressures, equally high molecular weight polymers were obtained. In all cases concentration of co-monomer incorporated into polymer was consistent with the amount of pressure and temperature of the polymerization run.

Table 9
Polymerizations with (**1**): FI(F_2I_2)$TiCl_2$ using 10-Undecen-1-ol as co-monomer.[a]

Lot #	Press. (psi)	Polymer (g)	(kg Pol/mmol cat/h)	IV (dl/g)	Mw[b] × 10^6 (g/mol)
17 287	100	20.0	2.2	30.4	8.7
17 292	200	28.5	3.1	37.1	11.7

[a] Polymerization conditions: 10 mg catalyst, 40 °C, 60 min runtime, Al/Ti = 2000, 10 ml undecyl-OH (comonomer).
[b] Calculated from IV.

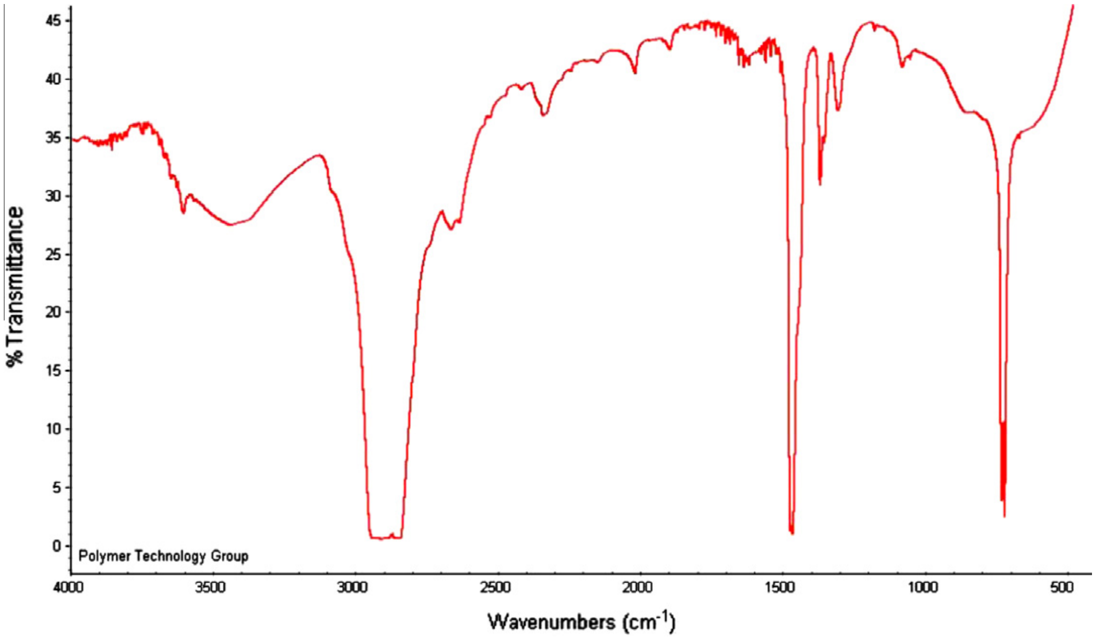


Fig. 3. FTIR of copolymerization product: 10-undecen-1-ol as co-monomer.

Table 10
Polymerizations with (**2**); FI(C_7tBu)$TiCl_2$.

Lot#	Catalyst (mg)	Al/Ti	Temp. (°C)	[PSI]	Time (min)	PE (g)	Activity gPE/mmol cat/h	IV (dL/g)
285.005	5	1785	25	40	10	4.0	3038	13.3
285.006	5	1786	25	40	20	5.0	1899	14.7
285.007	5	1786	25	40	40	13.0	2469	19.2
261/188	10	1785	50	100	30	15.5	3925	27.9
261/189	10	1785	50	100	60	35.1	4444	16.3
261/190	10	1785	50	100	90	37.5	3165	17.4
261/164	4	1131	60	300	60	70.0	8862	21.6

To further expand the utility of this catalyst system, co-polymerizations using functionalized olefins were performed using 10-undecen-1-ol as co-monomer (masked with aluminum alkyl). High molecular weight polymers were again obtained (Table 9), and the FTIR spectra (see Fig. 3) indicated the presence of hydroxy functionality being present (shoulder in the 3500–400 cm^{-1} region).

Polymerization using the titanium phenoxyimine system containing the cycloheptyl-imine and the more classic *tert*-butyl-phenoxy substitution displayed activities higher than those of (**1**), but with somewhat lower molecular weights (see Table 10). As with catalyst (**1**), increasing temperature causes an increase in the molecular weight of the polymer, also indicating the living nature of this catalyst system.

In order to further explore and leverage these catalyst systems, a complex having the combined features of the di-fluorine/di-iodo and the cycloheptyl was made (complex **3**). Polymerization results from the MAO activated complex (**3**) are included in Table 11.

Table 11
Polymerizations with (**3**); FI(C_7I_2)$TiCl_2$.

Lot#	Catalyst amount (mg)	Al/Ti	Temp. (°C)	Press. (psi)	Time (min)	PE (g)	Activity gPE/mmol cat/h	IV (dL/g)
170 589	8	3010	55	100	30	28.7	7562	17.5
180 552	10	1736	52	100	60	9	949	20.5

Catalyst activity and polymer molecular weight were intermediate between those of the FI catalyst (**1**) and the FI catalyst (**2**).

4. Conclusion

A group of catalysts capable of making UHMWPE were compared for productivity in homo and co-polymerizations. Classic Ziegler–Natta $TiCl_3$ type catalysts have low activity but produce UHMWPE at commercially relevant temperatures. The commercially available Mg/Si supported titanium catalyst (Sylopol®) produced extremely high molecular weight materials and had excellent activities. Metallocene catalysts in general required lower temperatures and higher pressures to produce acceptable molecular weights. The phenoxyimine catalysts tested produced a wide range of UHMWPE copolymers but activities were lower than expected for these single site catalyst systems.

Ziegler–Natta [16], metallocenes [17] and FI catalysts [18] are well-known in the academic literature as well as in patents [19]. Activities presented herein using just ethylene as monomer compare well with literature results; however, limited information is available on UHMWPE copolymer synthesis [4–7]. The ability to produce comonomer compositions having relevant composition distributions has been repeatedly shown to improve a number of properties such as fatigue and environmental stress crack resistance [9]. One method for producing UHMWPE copolymers having inverse comonomer distributions is to select catalysts having dissimilar reactivity ratios for comonomer insertion [20]. The ability to produce inverse distributed UHMWPE copolymers depends on the judicious selection of catalysts, their activities and ability to incorporate or exclude comonomer from the growing polymer chain. This survey provided a starting point for further development [21].

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