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Catalysts for UHMWPE

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Summary: Polyolefin coordination catalysts useful for producing UHMWPE are surveyed, including classic Ziegler-Natta (ZN), current commercial generation ZN, metallocene single site, and non-metallocene. Catalysts were prepared and compared for productivity and selected polymer properties under a variety of conditions. Classic catalysts used were long lived $TiCl_3$ crystalline metal clusters made by reducing $TiCl_4$ by co-crystallizing with aluminum alkyls. Data presented from the synthesis and polymerization with these catalysts shows temperature and molecular weight response that were expected for these systems. Commercially available titanium on silica/ magnesium chloride was activated with aluminum alkyls and had higher activity than those of the previous generation. Conditions for polymerizing supported metallocenes for producing polymers in the UHMWPE range were described. Long range "non-metallocenes" of the phenoxy-imine class were activated with MAO was tested and reported.

Keywords: metallocenes; non-metallocenes; polyolefin catalysts; UHMWPE

Introduction

Ultra high molecular weight polyethylene (UHMWPE) is one of the toughest plastics known having very high abrasion resistance and low coefficient of friction. It has found a variety of applications due to its remarkable properties.

Polyolefin synthesis and catalysis is a mature and well studied area. Generations of catalysts used for synthesizing polyolefins have been described by a number of authors.[1] The earliest generations consisted of titanium trichloride activated with aluminum alkyls and produced only a few kilograms of polymer per gram of catalyst. The residual content of catalyst and aluminum in the polymer was high enough to require post-reactor processing to deactivate the catalyst with alcohol and removal by distillation and stripping. For initial development of the commercial polyolefin field and up until about the year 2000, these types of catalyst systems were used for producing polyolefins, including polyethylene.

On the surface, the synthesis of these early catalysts appears quite simple but there are many different recipes and preparations reported. One entry into these materials is described as the controlled addition of a clear colorless solution of titanium tetrachloride to a solution containing aluminum alkyl, forming titanium trichloride which precipitates as a fine brown or purple sand.[3] The particles that are formed are a conglomerate of hexagonal crystallites of varying sizes, where the center, the middle, and the exterior of these particle conglomerates are composed of irregular arrangement of these crystallites. The average size of these surfaces is a population/ mixture of dimensions and there are a number of factors that effect the size and distribution of these crystallites and the size and the distribution of the final particles: the concentration of the reactants, the temperature of the addition, the speed of addition, the stirring speed effects on the aspect ratio, etc., all effect the resulting particle morphology. The polymer particles are replicated from the catalyst, and morphology of the polymer particles play an important role in final processing of this raw material into a usable part.

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Polymerizations with $TiCl_3$

$TiCl_3$ was synthesized as above fashion and activated with aluminum alkyl then used to polymerize ethylene to ultra high molecular weight at commercially relevant temperatures. *Experimental*: For polymerizations described in this paper which were carried out in a jacketed 4L 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 with continuous monomer feeding.

For polymerizations described in the 75L reactor, 50 L of heptane was used as the solvent; in some cases TiBAl was used as a scavenger. All other conditions were scaled up directly from the 4L reactor, except where indicated.

Molecular weight of the polymers was calculated from the intrinsic viscosity which was measured according to standard methods (ASTM D4020); comonomer composition was measured using FTIR methods (see ASTM D5576, D6248 and references therein).

In general, increasing polymerization temperature decreases polymer molecular weight (Table 1), and increasing pressure increases molecular weight. The system is not "living" since doubling the run time does not significantly increase the Mw. The molecular weight distribution of these catalysts is expected to be broad, due to the heterogeneous nature of the catalyst and the existence of multiple active sites in the catalyst.

For this catalyst system, hydrogen is an effective chain transfer/ polymer chain release agent, as are aluminum and many co-monomers. At equivalent temperatures as the concentration of hydrogen is increased from 2.1 to 8.5 mmol in the reactor there is a decrease in Mw from 4.3 MM down to 2.5 MM and an increase in mileage.

These polymers, because they are of such a high molecular weight, do not melt flow and processing is mainly through compression molding or *ram* extrusion. Solution viscosity is a related measure for the molecular weight.

The ability to create branching structures is possible and many different olefin monomers are co-reactive. Table 2 shows that UHMWPE is formed using $TiCl_3$ in the presence of a number of different comonomers. As these can also act as chain transfer agents, in general, we see a decrease in molecular weight with increasing comonomer concentration in the reactor with a slight increase in productivity.

Table 1.
Results from ethylene polymerizations using $TiCl_3$(a).

cat. [mg]	H_2 [mmol]	Temp [°C]	Press. [psi]	Time [min]	Polymer [g]	Mileage g PE/ g cat/min	IV [dL/g]	Mw x 10^{-6} [g/mol]
45	–	60	100	45	187	92.3	18.6	4.2
45	–	60	100	60	252	93.3	21.6	5.3
45	–	60	100	120	470	87.0	21.6	5.6
54	–	65	80	60	600	185.2	22.5	6.0
48	–	65	80	60	640	222.2	23.7	5.2
30	–	85	50	60	310	172.2	21.4	5.1
18	–	85	100	60	585	541.7	21.4	5.1
30	2.1	65	100	120	630	175.0	18.9	4.3
30	4.4	65	100	90	480	177.8	14.6	2.9
21	8.5	65	100	60	275	218.3	12.3	2.3
18	8.5	65	100	30	170	314.8	12.7	2.4

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

Table 2.
Results from ethylene co-polymerizations using $TiCl_3$.

Co-monomer [g]	cat. [mg]	temp [°C]	press [psi]	time [h]	Yield [g]	co-monomer mole %[b]	IV [dl/g]	Mw[c] × 10^{-6} [g/mol]
Hexene/[68]	67	65	100	5.0	345	6.0	19.0	3.6
Hexene/[75]	67	60	400	6.0	150	3.7	20.5	4.0
Hexene/[110]	67	65	120	6.0	315	7.0	10.9	1.7
Hexene/[122]	67	68	300	5.0	298	4.0		
Hexene/[68] 5MHD [a] / [5]	67	68	100	3.5	427	3.5	12.1	2.0
Propene[100]	67	59	200	4.0	400	9.0	18.1	3.4
Propene[100]	67	59	200	7.0	340	14.0	9.6	1.4
Propene[60]	33	60	400	4.5	290	6.5	23.1	4.7

[a] 5-methylhexadiene (5MHD).
[b] By ^{13}C-NMR.
[c] Calculated from intrinsic viscosity.

Polymerizations with Supported $TiCl_3$

For the early titanium trichloride catalysts the outer surfaces of the catalyst particle presented the majority of active sites for polymerization reactions. The center and the middle of the catalyst particle functioned as a carrier during the reactions and remained to be dealt with after the polymer was produced. In subsequent generations the interior of the catalyst particle was replaced with an inorganic support such as, magnesium chloride or silica, and reacted in such a way so that the supported particle disintegrated and became dispersed throughout the polymer particle as it is formed.

As described in a plethora of academic and patent literature the synthesis of silica or $MgCl_2$ supported titanium catalysts is not trivial and can involve many steps such as the controlled formation of spherical particles of magnesium via alcoholate support; the de-alcolation to varying levels of the support, the addition of titanium tetrachloride to the surface with subsequent washings, drying, and so forth. Many different groups have worked in the area of UHMWPE catalyst synthesis using the $TiCl_3$/ aluminum alkyl catalyst system.[3]

Table 3 contains examples of the polymerization results from a commercially available modified silica-magnesium chloride supported titanium complex designed specifically for the synthesis of polyethylenes for commercially relevant, commodity type of polymer.

This catalyst was activated with either DEAC or TiBAl and the catalyst loading in the reactor was varied along with pressure and temperature. As expected, increasing pressure or decreasing temperature increased the molecular weight of the polymer.

This particular catalyst system is used industrially with hydrogen to control the molecular weight and typically is operated at much higher temperatures than reported here; the activities are higher than for

Table 3.
Polymerization Results with Commercial ZN.

Cat.	Co-Cat	Reactor Conditions			Polymer [g]	Mileage	Molecular Mass	
amt [mg]	Type	Temp [°C]	Press [psi]	Time [h]		g Pol/g cat/h	IV [dl/g]	Mw[c] · 10^{-6} [g/mol]
5.5	DEAC	60	100	1	2.3	418	20.4	4.8
20.0	DEAC	60	100	1	15	750	20.2	4.7
20.0	DEAC	60	300	1	118	5900	22.5	5.5
30.0	TiBAl	40	300	1	250	8333	34.5	10.5
30.0	TiBAl	60	300	0.5	210	14000	19.9	4.6
57.0	TiBAl	60	300	0.5	243	8526	20.8	4.9
30.0	TiBAl	60	300	1	380	12667	22.9	5.7

the classic self-supported catalyst system. The highest Mw seen in the table here is ~10 million [g/mol] and varying conditions such as lower temperatures could increase this further.

ZN versus Single Site Catalysts (Metallocene)

For the classic Ziegler Natta catalysts the different reactive sites produce a composite polymer material consisting of a population of molecular chains having different chemical compositions and generally a broadened molecular weight.

Since the time Ziegler Natta catalysts were invented there were attempts to model the active sites by creating defined metallic centers which could be used to determine the mechanisms surrounding the polymerization chemistry. With the synthesis of titanocene dichloride in 1954,[4] metallocenes became available for testing. Natta, Breslow[5] and a number of pioneering workers examined this complex in olefin polymerizations. In the late 1970's commercial development became possible when Kaminsky discovered a key activator, methylalumoxane (MAO).[6] Metallocenes in general were further developed due to the pioneering work of Ewen and others who were looking for a method of increasing the molecular weight of copolymers while increasing co-monomer content.[7]

Metallocenes as single site catalysts give a uniform molecular weight distribution. Co-monomer incorporation across the molecular weight distribution is also more uniform, unlike the classic ZN catalysts where co-monomer predominates in lower molecular weight chains.

Metallocene Polymerizations

The synthesis of the metallocenes can be quite complicated and a number of structures have been reported with a range of activities, molecular weights, co-monomer incorporating abilities, etc.[8] Commercially available candidates were screened, including bis(ethylcyclopentadienyl)hafnocene dichloride, bis(n-butyl-cyclopentadienyl) hafnocene dichloride, bis indenyl hafnocene dichloride, ethylene bridged bis(indenyl)titanium, zirconium, hafnium dichlorides, and then even more exotic species such as ethylene bridged bis fluorene (metal)dichlorides, and the diphenylmethylenecyclopentadienyl-fluorene-zirconium dichloride. Some of these have been reported in the literature as capable of making high molecular weight linear polyethylenes and with good co-monomer incorporating ability.[9]

Ethylene bridged bis-fluorene zirconium dichloride, $Et(Flu)_2ZrCl_2$, produced polyethylene having a very high molecular weight (Figure 1). In a typical polymerization similar to those conditions described for the classic Ziegler Natta catalysts above at relevant polymerization temperatures and pressures between IV = 7

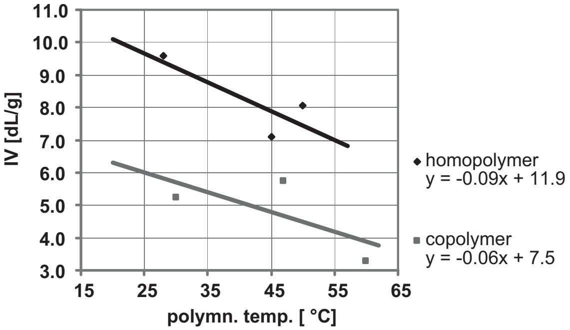

Figure 1.
Results from Homo and co-polymerizations using $Et(Flu)_2ZrCl_2^{a)}$.
a)see text for explanation of results.

(Mw ~ 900,000 g/mol) to IV = 10 (~2 MM g/mol) can be achieved. Co-polymerization results at identical temperatures produce polymers having lower molecular weight showing co-monomers are effective in lowering the molecular weight. For example at 60 °C, 100 psi ethylene pressure under these conditions, a polymer having 12 mol% butyl branches as measured by ^{13}C-NMR, was obtained however the Mw is only about ~330,000 [g/mol].

Molecular weight has been shown to be increased with hafnium complexes as compared to titanium or zirconium complexes and these were a logical choice as single site catalyst candidates for UHMWPE. Homogeneous polymerizations with $(EtCp)_2HfCl_2$ using hexane as a solvent and at varying temperatures and pressures using MAO as an activator at an aluminum to hafnium ratio of ~1200 and at 23 °C with increasing monomer concentration (increasing the ethylene pressure), increases Mw. Increasing the hexene concentration increased the catalyst activity and lowered the Mw [50 mls: 7%, 100 mls: 9% by ^{13}C-MAS NMR]. At 23 °C a polymer having a Mw of ~3.6 MM was produced making this catalyst system an interesting candidate for additional study.

One of our goals in polymerizations using these catalysts was to create an operations map to understand what are the conditions required for creating a polymer having a defined property under a set of controlled conditions. In Figure 2 we see a metallocene "map" with increasing temperatures and pressures and the resulting molecular weight, expressed in IV.

The morphology of the polymer produced in unsupported slurry metallocene polymerizations is generally unacceptable for commercial operation. Reactor fouling and low bulk density make processing difficult. Methods for supporting metallocenes include adsorption of the activated complex on calcined silica. These procedures are not trivial, and many methods have been described in the patent literature. We have developed similar formulations based on reported methods.

Results from a comparison of homogeneous vs. heterogeneous metallocene polymerizations done under similar conditions are shown in Figure 3. The supported metallocene makes a higher Mw polymer at the same temperature than the unsupported, for example, at about 40 °C the homogeneous polymer is formed having an IV of about 11.5 and the heterogeneous

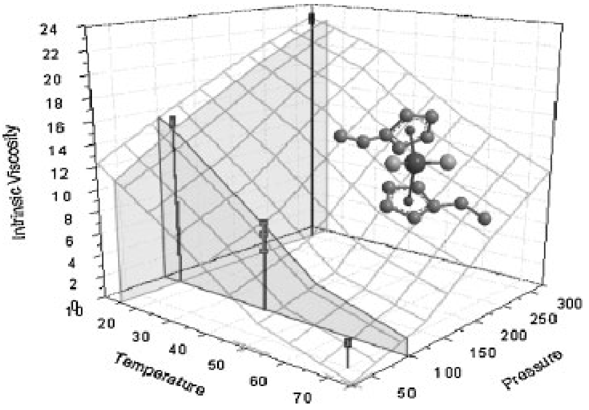

Figure 2.
Operation map for $(EtCp)_2HfCl_2^{a)}$.
$^{a)}$Polymerization conditions: homogeneous polymerization; 1 L stainless steel reactor; 2.5 L heptane (solvent), MAO Al//Hf ~ 1000; run time 1 h.

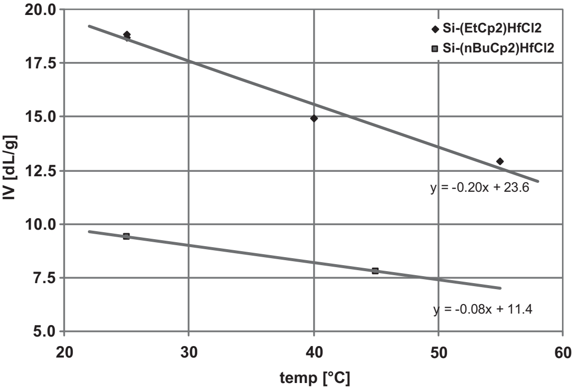

Figure 3.
Comparison of heterogeneous polymerizations with selected hafnocenes making UHMWPE[a].
[a]see text for explanation of results.

polymer has an IV of around 16. There are a number of reasons for this which are the supported catalysts have a lot less aluminum and therefore have less transfer to aluminum as a chain release mechanism.

We have scaled up these polymerizations to a 75 L reactor and under conditions identical to those in the 4L reactor and even sub-ambient. We are able to produce kilogram quantities of UHMWPE homo and co-polymers using supported single site catalysts for material and property evaluation. These polymers have good particle size distribution and molecular weight similar to those produced with the Zeigler Natta catalysts shown earlier.

Living Polyolefin Polymerizations: FI Type Single Site Candidates

Corradini described a number of "new century catalysts" including the Brookhart/Gibson late transition metal di-imines and tri-imines.[10] The FI catalysts originally discovered by the Mitsui[11] group and modified by Coates[12] represent a versatile set from this class. As with the metallocenes there are a number of different substitutions that can be made on these types of complexes. One of the more interesting catalysts reported by Weiser[13] contains a fluorinated phenyl group on the imine side of the molecule married with iodine substitutions on the phenoxy side.

Table 4.
Results from homogeneous polymerizations using FI(F2I2)$TiCl_2$[a].

CONDITIONS					RESULTS			
cat.	Co-Monomer		Reactor		Polymer [g]	Activity [g Pol/mmol cat/h]	Molecular Mass	
Amt [mg]	ID	Amt	Temp [°C]	Time [min]			IV [dl/g]	Mw[c] $\times 10^{-6}$ [g/mol]
20	–	0	31	60	39.0	2124	33.0	9.8
6	–	0	50	30	12.0	4356	28.2	7.8
10	–	0	51	60	6.0	653	25.9	6.9
20	Hexene	25	31	60	42.5	2314	35.3	10.9
10	Hexene	25	31	60	10.5	1143	36.3	11.3
10	Hexene	25	49	60	10.0	1089	30.3	8.6
10	Hexene	50	49	120	13.0	708	35.4	10.9

[a]see text for explanation of results.

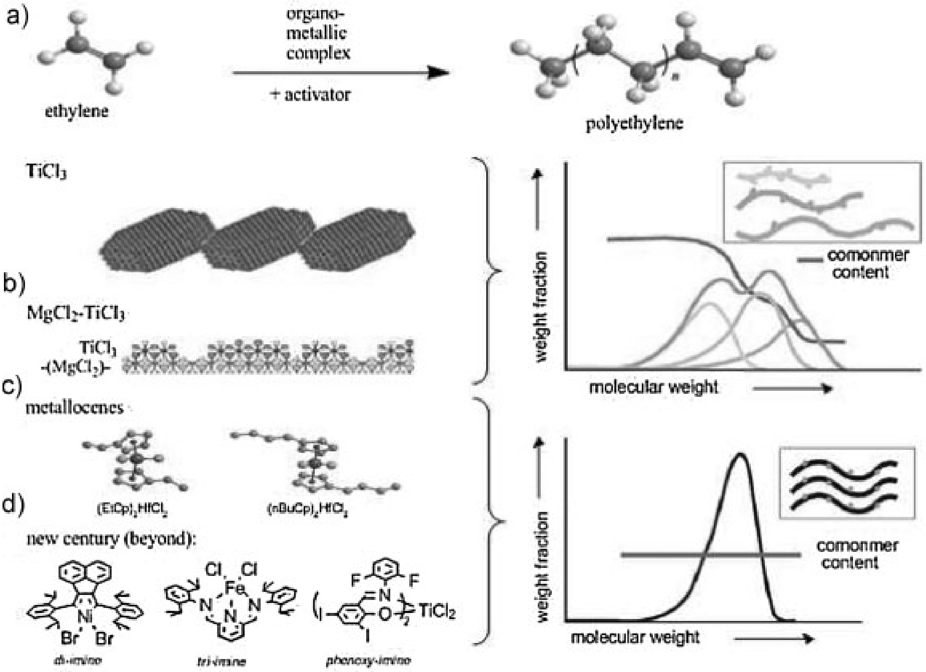

Figure 4.
Reaction scheme and molecular weight distribution of related catalyst families.

The result was described as a living catalytic complex capable of making UHMWPE. Synthesis of the complex (bis-(N-(3,5-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride) was prepared according to the literature. In our hands, under increasing pressures extremely high Mw polymers were produced with relatively little decrease in Mw with co-monomer addition (Table 4). At 45 °C, 100 psi, 60 min with 25 ml of hexene the polymer was found to contain 5.3% butyl branches by ^{13}C-NMR.

Discussion

A general reaction scheme for the experiments carried out is included in Figure 4. Catalysts having multiple reaction sites (heterogeneous catalysts) give rise to a mixture of different polymer chains and therefore a broad molecular weight distribution. Classic Ziegler Natta (ZN) (crystallites of $TiCl_3$, Figure 4a) and magnesium or silica (for example, Figure 4b) supported ZN are composed of reactive sites having reactive metals in different ligand environments. Single site catalysts such as the metallocenes (Figure 4c) or “new century” catalysts such as the di-imines, tri-imines, phenoxy-imines, etc. (Figure 4d), have identical ligand environments and produce a more homogeneous blend of polymer chains.[14]

The two main chain transfer reactions for chain termination in olefin catalyzed polymerizations are β-hydride elimination and chain transfer to aluminum. The suppression of β-hydride elimination to form ultra high molecular weight polyethylene was accomplished for metallocenes at increasing reaction pressure and reducing temperatures. Limiting the amount of aluminum added to the reactor also has a significant effect on increasing molecular weight for all catalyst systems. Comonomer addition is also an effective chain transfer agent.[14]

Conclusions

Different generations and classes of coordination catalysts have been presented that can be used for making UHMWPE. Suitable candidates have been tested and for a given macromolecular structure, the operations parameters such as temperature, pressure, kinetics, etc. required to exploit the catalyst and manipulate the system were determined. With the intent of eventually modifying the polymer properties with, for example co-monomers, and through manipulating the physical characteristics of the system we intend to produce a more suitable, substantial, and optimized product, which is the subject of continuing study.

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