(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 April 2011 (07.04.2011)

PCT

(10) International Publication Number
WO 2011/040958 A1

(51) **International Patent Classification**:
C08F 10/00 (2006.01) ***C08F 4/635*** (2006.01)
C08F 4/631 (2006.01) ***C08F 4/629*** (2006.01)

(21) **International Application Number**:
PCT/US2010/002637

(22) **International Filing Date**:
29 September 2010 (29.09.2010)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
12/587,187 2 October 2009 (02.10.2009) US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

WO 2011/040958 A1

(54) **Title**: PYRIDAZINE-MODIFIED ZIEGLER-NATTA CATALYST SYSTEM

(57) **Abstract**: A modified Ziegler-Natta catalyst system, a method for preparing the catalyst system, and a process for polymerizing an olefin in the presence of the catalyst system are disclosed. The catalyst system comprises a titanium or vanadium compound, an aluminum compound, and a pyridazine. Improved properties such as increased molecular weight and narrowed molecular weight distribution are obtained.

PYRIDAZINE-MODIFIED ZIEGLER-NATTA CATALYST SYSTEM

FIELD OF THE INVENTION

This invention relates to a modified Ziegler-Natta catalyst system. The catalyst system includes a pyridazine, which influences polyolefin properties such as molecular weight.

BACKGROUND OF THE INVENTION

Interest in catalysis continues to grow in the polyolefin industry. Many olefin polymerization catalysts are known, including conventional Ziegler-Natta catalysts. To improve polymer properties, single-site catalysts, in particular metallocenes are beginning to replace Ziegler-Natta catalysts. Single-site catalysts typically require large amounts of expensive activators such as methylalumoxane or salts of non-nucleophilic anions such as triphenylcarbenium tetrakis(pentafluorophenyl)borate. It would be desirable to improve polyolefin properties without the high cost of single-site catalysts and their activators.

Ziegler-Natta catalyst systems are well known in the art. Useful Ziegler-Natta catalysts include titanium or vanadium compounds and their combinations with aluminum compounds. In some circumstances, mixtures are preferred (U.S. Pat. Nos. 3,218,266, 4,483,938, 4,739,022, and 5,492,876 use mixtures of vanadium and titanium-based Ziegler-Natta catalysts), but commonly a single titanium or vanadium compound is used. It is known to support the titanium or vanadium compound with compounds such as silica or magnesium chloride and considerable research has been done in this area. Known compositions also include an aluminum compound, sometimes referred to as a cocatalyst. Trialkyl aluminums, dialkyl aluminum halides, and alkyl aluminum dihalides are common cocatalysts.

It is known to add other compounds to a Ziegler-Natta catalyst system to influence catalytic properties. Various Lewis bases have been used; they are often referred to as modifiers or electron donors. When the electron donor is added during the preparation of the Ziegler-Natta catalyst system it is sometimes called an "internal donor," while those added during or immediately prior to the polymerization have been called "external donors." A variety of electron donors have been

disclosed (for example, see U.S. Pat. No. 4,136,243). Common electron donors include ethers and esters (for example, see U.S. Pat. No. 5,968,865), but many others have been used. U.S. Pat. No. 5,106,926 gives examples of suitable electron donors as alkyl esters of aliphatic or aromatic carboxylic acids, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl or cycloalkyl ethers, and mixtures thereof with tetrahydrofuran being preferred. U.S. Pat. No. 4,927,797 discloses the use of silane donors such as methylcyclohexyldimethoxysilane. Sometimes two or more electron donors are used. U.S. Pat. No. 7,560,521 teaches a combination of a monofunctional donor selected from ethers, esters, amines, or ketones with a difunctional donor selected from diesters, diketones, diamines, or diethers.

U.S. Pat. No. 6,436,864 discloses unsaturated nitrogenous compounds as electron donors for Ziegler-Natta catalysts. The nitrogenous compound has the formula A-$(L)_m$-A' where A is a "first coordinating segment containing a coordinating nitrogen atom within a C=N group," L is a linking group, and A' is a "second coordinating group containing a second coordinating atom selected from the group consisting of N, O, S, and P" (see col. 4, ll. 10-25). The reference contemplates that A might be a pyridazinyl group (col. 10, formula (II) and ll. 37-45). Pyridazine compounds that lack the second coordinating group are not suggested. An imine, a diimine, and a methoxymethylpyridine are used in the examples.

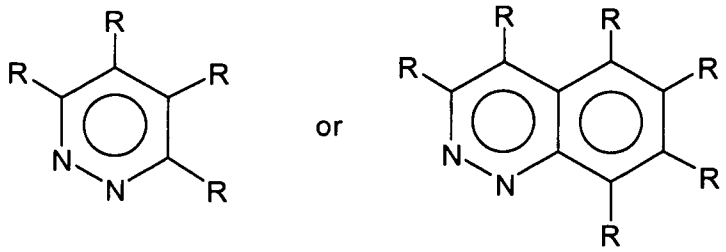
Pyridazinyl groups have also been disclosed as components of single-site catalysts. For instance, U.S. Pat. No. 7,202,373 teaches monocyclopentadienyl single-site complexes in which a pyridazine moiety such as a cinnoline group might be fused to the cyclopentadienyl ring. Coordination to the metal is through the Cp ligand. U.S. Pat. No. 7,507,782 teaches transition metal complexes in which a neutral tridentate ligand coordinates with the transition metal using three nitrogen atoms. The nitrogen-containing groups of the ligand may be fused to a cinnoline moiety (col. 4, ll. 43-44) in these single-site complexes. U.S. Pat. No. 6,355,746 teaches complexes of mid-transition metals (including vanadium) and unsaturated nitrogenous ligands as single-site catalysts; in these catalysts, cinnoline (col. 12, l. 21) is described as a possible ancillary ligand (identified as L^A or L^B). In addition, the single-site complex (formula (I), co. 11) can utilize a pyridazinyl group as part of a bidentate ligand (L^1) that also bonds to the metal using a N, O, S, or P atom from a

second coordinating group (see col. 11, esp. ll. 32-35 and 60-65). None of these references uses a pyridazine to modify a Ziegler-Natta catalyst system.

The role of donors is not completely understood and remains a subject of continued research. As polyolefin applications become more demanding, there is a continued need for improvements in catalyst systems. Despite the considerable research that has been done in this area, apparently no one has studied simple pyridazine compounds as components of a Ziegler-Natta catalyst system.

SUMMARY OF THE INVENTION

In one aspect, the invention is a modified Ziegler-Natta catalyst system and a method for preparing the catalyst system. In another aspect, the invention is a process for polymerizing an olefin in the presence of the catalyst system. The catalyst system comprises a titanium or vanadium compound, an aluminum compound, and a pyridazine having the structure:



wherein each R is independently H, Cl, Br, or C_1-C_{16} hydrocarbyl and wherein two adjacent R groups may be joined together to form a ring. The catalyst system enables improved polyolefin properties such as increased molecular weight and narrowed molecular weight distribution.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a modified Ziegler-Natta catalyst system comprising: (a) a titanium or vanadium compound; (b) an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (c) a pyridazine. The titanium or vanadium compound can be any compound normally effective as a Ziegler-Natta catalyst. Preferred titanium compounds include titanium halides such as titanium trichloride and titanium tetrachloride, and titanium alkoxides such as titanium(IV) butoxide. Preferred vanadium compounds include vanadium halides such as vanadium tetrachloride, vanadium oxyhalides such as vanadium oxytrichloride, and vanadium

alkoxides such as vanadium(V) oxytriethoxide. Mixtures of titanium compounds and vanadium compounds may be used.

More preferably, titanium tetrachloride is used. When titanium tetrachloride is used, it is preferably supported on or modified with a magnesium compound. Many magnesium compounds suitable for use in supporting or modifying the Ziegler-Natta catalysts are well known. Examples include magnesium chloride, alkyl magnesium halides, and magnesium siloxanes. For additional examples, see U.S. Pat. Nos. 4,298,718, 4,399,054, 4,495,338, 4,464,518, 4,481,301, 4,518,706, 4,699,961, 5,258,345, 6,291,384, and 7,560,521, the teachings of which are incorporated herein by reference.

Optionally, a Lewis base is included in the catalyst system. Preferred Lewis bases are C_3-C_{24} esters such as butyl acetate, diethyl phthalate, trimethyl trimellitate, and diethyl adipate and C_4-C_{16} ethers such as dibutyl ether, glyme, and diglyme. More preferred Lewis bases are C_9-C_{24} esters such as diethyl phthalate, dioctyl isophthalate, and 1,6-hexanediol bisbenzoate.

In one aspect, the titanium compound is a titanium halide supported on magnesium chloride, and the Lewis base, if any, is present in a Lewis base/Ti molar ratio less than 1. The supported titanium compound preferably has as a porosity (P_F) determined with the mercury method higher than 0.3 cm^3/g, and typically in the range of 0.50-0.80 cm^3/g. The total porosity (P_T) is usually in the range of 0.50-1.50 cm^3/g, preferably from 0.60-1.20 cm^3/g. The surface area measured by the BET method is preferably lower than 80, more preferably from 10 to 70 m^2/g. The porosity measured by the BET method is generally from 0.10 to 0.50, preferably from 0.10 to 0.40 cm^3/g.

Particles of the magnesium chloride-supported titanium compound preferably have substantially spherical morphology. Average diameters are preferably from 5 to 150 μm, more preferably from 20 to 100 μm. "Substantially spherical" particles are those wherein the ratio between the major axis and minor axis is less than or equal to 1.5, preferably less than 1.3.

The titanium compound preferably has the formula $Ti(OR^{II})_nX_{y-n}$, wherein n has a value from 0 to 0.5, y is the valence of titanium, R^{II} is a C_1-C_8 alkyl, cycloalkyl or aryl radical, and X is halogen. Preferably, R^{II} is ethyl, isopropyl, n-butyl, isobutyl,

2-ethylhexyl, n-octyl, phenyl, or benzyl; X is preferably chlorine. $TiCl_4$ is especially preferred.

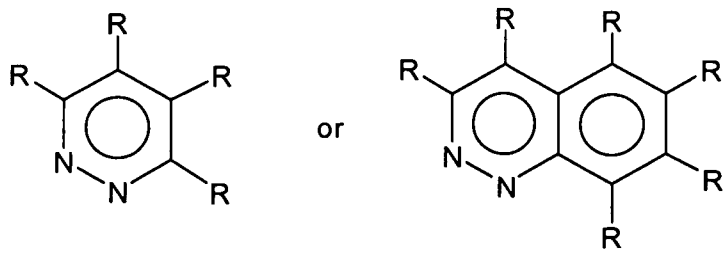
One method suitable for preparing the spherical components mentioned above comprises a first step in which a compound $MgCl_2.mR^{III}OH$, wherein $0.3 \leq m \leq 1.7$ and R^{III} is a C_1-C_{12} alkyl, cycloalkyl or aryl radical, reacts with the titanium compound of formula $Ti(OR^{II})_nX_{y-n}$.

The compounds are conveniently obtained by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct with stirring at the melting temperature of the adduct (100-130°C). The emulsion is quickly quenched, and the adduct solidifies as spherical particles. Suitable methods for preparing the spherical adducts are disclosed, e.g., in U.S. Pat. Nos. 4,469,648 and 4,399,054, the teachings of which are incorporated herein by reference. Another useful method for making the spherical components is spray cooling, described, e.g., in U.S. Pat. Nos. 5,100,849 and 4,829,034.

For more examples of suitable titanium compounds and their methods of preparation, see U.S. Pat. Nos. 4,399,054 and 6,627,710, the teachings of which are incorporated herein by reference.

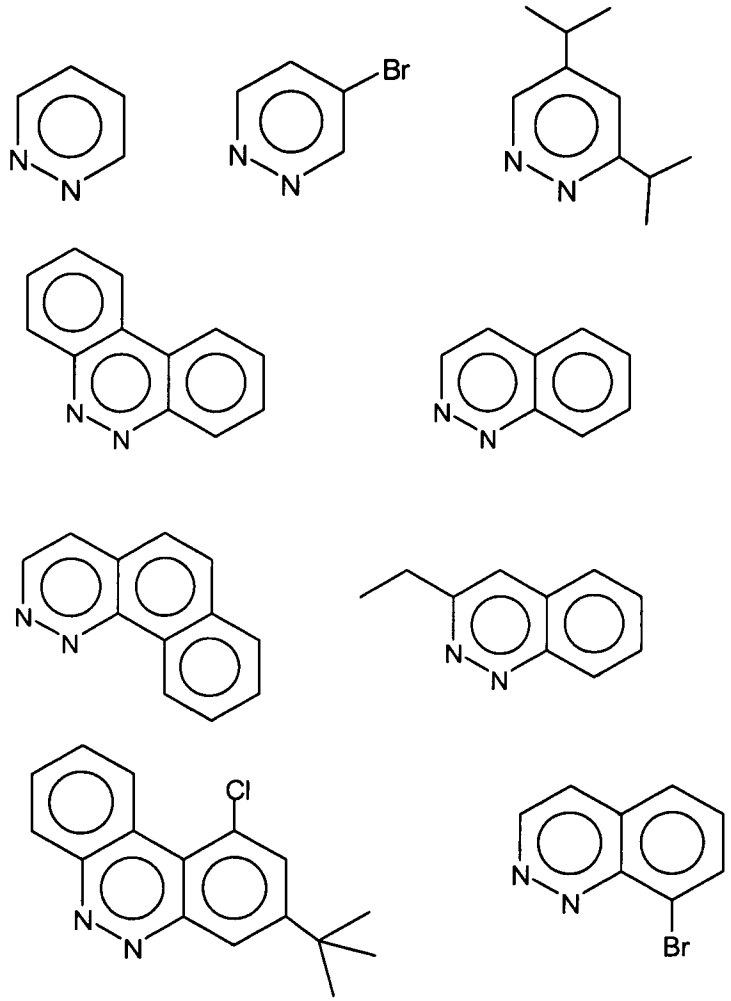
The modified Ziegler-Natta catalyst system includes an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof. Suitable aluminum compounds include triethylaluminum, tri-isobutylaluminum, diethylaluminum chloride, butylaluminum dichloride, and the like, and mixtures thereof. Trialkyl aluminum compounds are preferred. Preferably, the molar ratio of the aluminum compound to titanium compound is within the range of 0.5:1 to 500:1.

The modified Ziegler-Natta catalyst system includes a pyridazine. Suitable pyridazines have the structure:



wherein each R is independently H, Cl, Br, or C_1-C_{16} hydrocarbyl and wherein two adjacent R groups may be joined together to form a ring. Preferably, the pyridazine is a cinnoline, e.g., benzo[c]cinnoline.

Some examples of suitable pyridazines are shown below:



Some pyridazines are commercially available; others can be prepared using a variety of methods known in the art. Pyridazines are most commonly prepared starting from carbonyl compounds, acids, lactones, anhydrides, carbohydrates, or other heterocycles. They can also be produced using cycloaddition reactions. Suitable synthetic approaches are discussed in review articles by M. Tišler and B. Stanovnik, Advances in Heterocyclic Chemistry 9 (1968) pp. 211-242 and 24 (1979) pp. 363-394, and references cited therein. Preferably, the molar ratio of the pyridazine to titanium or vanadium compound is within the range of 1:1 to 50:1, more preferably from 10:1 to 30:1.

The modified Ziegler-Natta catalyst system is useful for polymerizing olefins. Preferably, the olefin is an α-olefin. Preferred α-olefins are ethylene, propylene, 1-butene, 1-hexene, 1-octene, and mixtures thereof. More preferred are ethylene, propylene, and combinations of ethylene with propylene, 1-butene, 1-hexene, or 1-

octene. When ethylene is polymerized in combination with another α-olefin, the modified Ziegler-Natta catalyst system produces polyethylene with good incorporation of the α-olefin. The amount of α-olefin incorporation will depend upon the particular α-olefin and the amount added to the polymerization. The level of α-olefin incorporation can be easily measured by FT-IR spectroscopy. Each molecule of α-olefin incorporated gives one tertiary carbon atom.

The modified Ziegler-Natta catalyst system is useful for preparing polyolefins with increased molecular weight. For some applications, a polyolefin with a high molecular weight, in particular, a high weight average molecular weight (M_w) is needed. M_w has a pronounced effect on melt flow properties. One measure of melt flow is melt index (MI) where the amount of polyolefin that flows through an orifice is measured as a function of time. Generally, MI decreases with increasing M_w. The modified Ziegler-Natta catalyst system is useful for preparing polyolefins with a low MI. Polydispersity is the ratio of weight average molecular weight to number average molecular weight (M_w/M_n). For certain applications, a narrow molecular weight distribution (low polydispersity) is desired. It can be difficult to obtain low polydispersity with Ziegler-Natta catalysts, but the modified Ziegler-Natta catalyst system is useful for preparing polyolefins with reduced polydispersity.

Optionally, hydrogen is used to regulate polyolefin molecular weight. The amount of hydrogen needed depends upon the desired polyolefin molecular weight and melt flow properties. Generally, as the amount of hydrogen is increased, the polyolefin molecular weight decreases and the melt index increases.

The polymerizations are normally conducted under pressure. The pressure is preferably in the range of 0.2 MPa to 35 MPa, more preferably from 0.4 MPa to 25 MPa.

Many types of polymerization processes can be used, including gas phase, bulk, solution, or slurry processes. The polymerization can be performed over a wide temperature range. Generally, lower temperatures give higher molecular weight and longer catalyst lifetimes. However, because the polymerization is exothermic, lower temperatures are more difficult and costly to achieve. A balance must be struck between these two factors. Preferably, the temperature is within the range of 0°C to 150°C. A more preferred range is from 20°C to 90°C.

Catalyst concentrations used for the olefin polymerizations depend on many factors. Preferably, however, the concentration ranges from 0.01 micromoles titanium or vanadium compound per liter to 100 micromoles per liter. Polymerization times depend on the type of process, the catalyst concentration, and other factors. Generally, polymerizations are complete within several seconds to several hours.

The modified Ziegler-Natta catalyst system can be made by any suitable method; those skilled in the art will recognize a variety of acceptable synthetic strategies. Each component can be separately added to the polymerization reactor. Preferably, two or more components are combined prior to addition. For example, the pyridazine may be reacted with the titanium or vanadium compound prior to addition to the polymerization reactor. In one preferred method, the pyridazine is reacted with the aluminum compound prior to addition to the reactor. More preferably, the pyridazine is reacted with the aluminum compound and the reaction mixture is contacted with a titanium or vanadium compound. This mixture is then added to the polymerization reactor. Most preferably, the pyridazine is reacted with the aluminum compound and the reaction mixture is contacted with a titanium compound that has been supported on a magnesium compound, especially magnesium chloride.

The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

EXAMPLE 1

Modified Ziegler-Natta Catalyst System

A magnesium chloride and ethanol adduct is prepared following the method described in Example 2 of U.S. Pat. No. 4,399,054, but working at 2000 RPM instead of 10,000 RPM. The adduct is treated thermally under a nitrogen stream, over a temperature range of 50-150°C, until a weight content of 25% of ethanol is reached. In a 2-L four-neck flask, purged with nitrogen, $TiCl_4$ (1 L) is charged at 0°C followed by the spherical $MgCl_2$/ethanol adduct (70 g). The temperature is raised to 130°C in 2 hours and maintained for 1 hour. The stirring is discontinued, the solid product is allowed to settle, and the supernatant liquid is removed by siphoning.

Fresh $TiCl_4$ is charged to the flask, the temperature is brought to 110°C and maintained for 60 minutes. The stirring is discontinued, the solid product is allowed to settle, and the supernatant liquid is removed by siphoning. The solid residue is washed once with heptane at 80°C, five times with hexane at 25°C, dried under vacuum at 30°C, and analyzed. The resulting solid contains 3.5% by weight titanium.

Benzo[c]cinnoline (4×10^{-4} mole) is added to a solution of triethylaluminum (4×10^{-4} mole) in hexanes. The solution is stirred for 1 hour and 20 mg (2×10^{-5} mole Ti) of titanium tetrachloride supported on magnesium chloride (prepared as described above) is added. The mixture is stirred for 30 minutes and used as described below in an olefin polymerization.

EXAMPLE 2

Polymerization

Isobutane (1 L), 1-butene (20 mL), and 1M triethylaluminum solution in hexanes (4 mL) are added to a dry, stainless-steel 2-L autoclave reactor. The reactor is heated to 80°C and hydrogen is added from a 300-mL vessel at 4.10 MPa to effect a pressure drop of 0.34 MPa. The reactor is pressurized to 0.7 MPa with ethylene. The polymerization reaction is started by injecting the modified catalyst system from Example 1. The temperature is maintained at 80°C and ethylene is supplied on demand to maintain the reactor pressure of 0.7 MPa. After 64 minutes, the polymerization is terminated by venting the autoclave. The resulting polyethylene is dried and tested.

Yield: 46 g. Activity: 2100 g polyethylene per g supported titanium compound per hour. By GPC, the polyethylene has a weight-average molecular weight (M_w) of 193,000 and a M_w/M_n of 6.0. Branching (by FT-IR spectroscopy): 6.0 tertiary carbons per 1000 carbons. Percent crystallinity (by differential scanning calorimetry): 55%. Melt index (MI, measured according to ASTM D-1238, Condition E): 0.20 dg/min. Rheological testing is performed, and ER, an elasticity parameter measured according to ASTM D4440-95A (and as described in U.S. Pat. Nos. 5,534,472 and 6,713,585 and in R. Shroff and H. Mavridis, J. Appl. Polym. Sci. 57 (1995) 1605), is 2.4.

COMPARATIVE EXAMPLE 3

The polymerization of Example 2 is repeated, but with a catalyst system that does not contain benzo[c]cinnoline. The system is prepared by adding 20 mg (2 x 10^{-5} mole Ti) of the same titanium compound to a solution of triethylaluminum (4 x 10^{-4} mole) in hexanes. The results are shown in Table 1.

COMPARATIVE EXAMPLE 4

The polymerization of Example 2 is repeated, but with a catalyst system that uses indazole (4 x 10^{-4} mole) as a replacement for benzo[c]cinnoline. The results are shown in Table 1.

Table 1

Polymerizations

Ex.	Time (min)	Activity	MI	M_w	M_w/M_n	Branches /1000 C	Crystallinity (%)	ER
2	64	2100	0.20	193,000	6.0	7.0	55	2.4
C3	30	8800	2.6	134,000	7.8	11.7	53	2.4
C4	51	2900	4.8	115,000	7.9	17.7	46	3.2

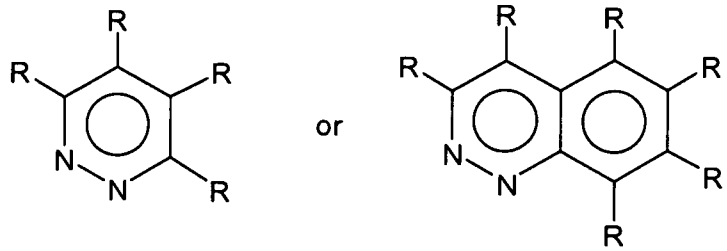
Example 2 shows that the use of a pyridazine, in this case benzo[c]cinnoline, provides increased molecular weight. The M_w of this polymer is higher than that of the polyolefin made without benzo[c]cinnoline (Comparative Example 3). Use of the pyridazine provides a more than 40% increase in M_w. Comparative Example 4 shows that this is an unexpected result, as indazole, another heterocyclic 1,2-diaza compound has the opposite effect on M_w.

Example 2 shows that the use of a pyridazine also provides lower polydispersity. With benzo[c]cinnoline, the polydispersity (M_w/M_n) is 6.0; the polydispersity is 7.8 in the control experiment without benzo[c]cinnoline (Comparative Example 3). Comparative Examples 4 shows that indazole fails to provide a similar effect on polydispersity.

The preceding examples are meant only as illustrations. The following claims define the invention.

We claim:

1. A modified Ziegler-Natta catalyst system comprising: (a) a titanium or vanadium compound; (b) an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (c) a pyridazine having the structure:



wherein each R is independently H, Cl, Br, or C_1-C_{16} hydrocarbyl and wherein two adjacent R groups may be joined together to form a ring.

2. The catalyst system of claim **1** wherein the titanium or vanadium compound is selected from the group consisting of titanium halides, titanium alkoxides, vanadium halides, vanadium oxyhalides, vanadium alkoxides, and combinations thereof.

3. The catalyst system of claim **1** wherein each R is H.

4. The catalyst system of claim **1** wherein the pyridazine is benzo[c]cinnoline.

5. The catalyst system of claim **1** wherein the molar ratio of pyridazine to titanium or vanadium is from 50:1 to 1:1.

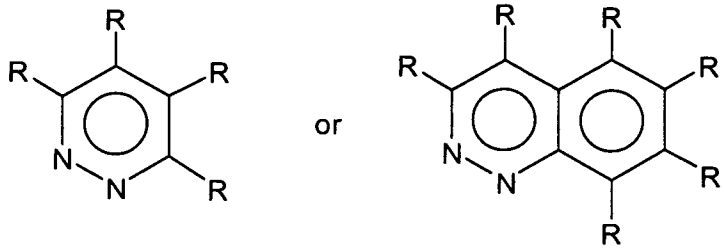
6. A process which comprises polymerizing an olefin in the presence of the catalyst system of claim **1**.

7. The process of claim **6** wherein the olefin is selected from the group consisting of ethylene, propylene, 1-butene, 1-hexene, 1-octene, and combinations thereof.

8. A method for preparing a modified Ziegler-Natta catalyst system, said method comprising: (a) reacting a pyridazine with an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (b) contacting the reaction mixture from step (a) with a titanium or vanadium compound.

9. A process which comprises polymerizing an olefin in the presence of a modified Ziegler-Natta catalyst system prepared by the method of claim **8.**

10. A modified Ziegler-Natta catalyst system comprising the product obtained by contacting: (a) a titanium or vanadium compound; (b) an aluminum compound selected from the group consisting of trialkyl aluminums, dialkyl aluminum halides, alkyl aluminum dihalides, and combinations thereof; and (c) a pyridazine having the structure:



wherein each R is independently H, Cl, Br, or C_1-C_{16} hydrocarbyl and wherein two adjacent R groups may be joined together to form a ring.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/002637

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F10/00 C08F4/631 C08F4/635 C08F4/629
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 118 767 A (JOB ROBERT C [US]) 2 June 1992 (1992-06-02)	1-3,5-10
Y	claim 1 column 6, line 6 - line 7	4
Y	US 7 371 866 B2 (JARY WALTHER [AT] ET AL) 13 May 2008 (2008-05-13) column 2, line 22 - line 35	4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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Date of the actual completion of the international search	Date of mailing of the international search report
17 December 2010	23/12/2010

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/002637

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