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(54) Title: POLYMERS, METHOD OF PRODUCING THE SAME, AND ARTICLES MADE THEREFROM

(57) Abstract: A virgin granular polymer comprising polymer particles wherein at least 90% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1, and further wherein the virgin granular polymer has an I_{21} less than or equal to (70) and/or further wherein at least 90% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001, and further wherein the virgin granular polymer has an I_{21} less than or equal to (70) is provided.

POLYMERS, METHOD OF PRODUCING THE SAME, AND ARTICLES MADE THEREFROM

Field of the Invention

The invention relates to polymers, method of producing the polymer and articles made therefrom. More particularly, the invention relates to polymers having a narrow composition distribution across particle size and providing low gels and good visual appearance when used to make articles.

Background of the Invention

Fluidized bed and slurry polymerization systems, particularly staged reactor systems, can suffer from significant variation in the polymer properties of varying particle size fractions. Large variations in polymer properties across particle size can lead to difficulty in mixing the different particles during, for example, pelletization. If all of the granular particles are of similar properties, mixing will occur readily. However, if one or more fractions of particles are of substantially different molecular weight or density, melting during a pelleting operation will not be uniform. Nonuniform pelletization can, in turn, result in:

1. "unmelts" - pellets that still have some areas of relatively undispersed granular which may cause gels or imperfections in finished articles;
2. very high gel count pellets which can occur when granular particles are of significantly different viscosity when melted, i.e. a large molecular weight variation across particles, leading to very high gel counts in thin sheets or films; and
3. an inability to use the resin in granular form as exiting from the final reactor due to substantial differences in molecular weight or density that prevent direct granule users, such as rotational molders, or fabricating extruders, such as blow molders, from utilizing the product due to poor mixing and high gel counts.

Such variation in polymer properties across particle size fractions occur more significantly when dual or linked reactors are used in the polymerization process, giving an even greater potential for formation of polymer granules with widely divergent properties. For example, if the polymer exiting the first reactor substantially differs in polymer properties across the particle size range, this disparity will continue and be further exacerbated in the second reactor.

To address this situation, the current approach is to employ very small catalyst particles which will produce very small polymer particles. Once used in applications, these very small polymer particles do not appear as a gel even with broad compositional distributions.

A catalyst system useful across a broad range of catalyst particle size and which produces polymers that may be compounded to produce very low gel counts would be very desirable.

Summary of the Invention

The instant invention is a polymer, a method of producing the polymer and articles made from the polymer.

In one embodiment, the instant invention provides a virgin granular polymer comprising polymer particles wherein at least 90% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1, and further wherein the virgin granular polymer has an I_{21} less than or equal to 70.

In another embodiment, the instant invention provides a virgin granular polymer comprising polymer particles wherein at least 90% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001, and further wherein the virgin granular polymer has an I_{21} less than or equal to 70.

In another embodiment, the invention provides a reaction product of polymerizing at least one olefin monomer in the presence of: (A) at least one catalyst precursor produced by contacting a Group 4 metal compound with one or more Titanium compounds selected from the group of $TiCl_3$ (Al-activated or hydrogen-reduced), and

$Ti(OR)_4$ where R is ethyl, isopropyl or n-butyl in the presence of an alcohol solution comprising at least one C_2-C_4 alcohol and at least one of $MgCl_2$ and magnesium compounds which form $MgCl_2$ in the presence of the alcohol solution to form a catalyst precursor solution, forming said catalyst precursor solution into solid particles and subsequently halogenating the solid particles; and (B) at least one co-catalyst; wherein the reaction product comprises a granular polymer comprised of polymer particles and further wherein at least 90% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

In another embodiment, the instant invention provides a reaction product of polymerizing at least one monomer, in the gas phase, in the presence of: (A) at least one catalyst precursor produced by contacting a Group 4 metal compound with one or more Titanium compounds selected from the group of $TiCl_3$ (Al-activated or hydrogen-reduced), and $Ti(OR)_4$ where R is ethyl, isopropyl or n-butyl in the presence of an alcohol solution comprising at least one C_2-C_4 alcohol and at least one of $MgCl_2$ and magnesium compounds which form $MgCl_2$ in the presence of the alcohol solution to form a catalyst precursor solution, forming said catalyst precursor solution into solid particles and subsequently halogenating the solid particles; and (B) at least one co-catalyst; wherein the reaction product comprises a granular polymer comprised of polymer particles and further wherein at least 90% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product , in accordance with any of the preceding embodiments, except that at least 95% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product , in accordance with any of the preceding embodiments, except that at least 93% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product , in accordance with any of the preceding embodiments, except that at least 95% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product , in accordance with any of the preceding embodiments, except that at least 93% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product , in accordance with any of the preceding embodiments, except that the granular polymer is produced in a two stage linked reactor system.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product, in accordance with any of the preceding embodiments, except that the granular polymer is produced in a one stage reactor system.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product, in accordance with any of the preceding embodiments, except that the granular polymer is produced in a fluidized bed reactor system.

In an alternative embodiment, the instant invention provides a virgin granular polymer and reaction product, in accordance with any of the preceding embodiments, except that the granular polymer is produced in a slurry reactor system.

In an alternative embodiment, the instant invention provides a virgin granular polymer consisting essentially of polymer particles wherein at least 90% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1, and further wherein the virgin granular polymer has an I_{21} less than or equal to 70.

In another embodiment, the instant invention provides a virgin granular polymer consisting essentially of polymer particles wherein at least 90% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001, and further wherein the virgin granular polymer has an I_{21} less than or equal to 70.

Detailed Description of the Invention

The terms “catalyst” and “catalyst composition” as used herein, refer to transition metal compounds, or mixtures thereof, that are useful in catalyzing the polymerization of addition polymerizable monomers, generally in combination with one or more cocatalysts or activator compounds. Preferred catalysts are mixtures or complexes of non-metallocene transition metal compounds and magnesium compounds, such as magnesium chloride compounds, alternatively referred to as Ziegler Natta catalysts or Ziegler Natta type catalysts.

The term “procatalyst” as used herein means a catalyst composition ready to be injected or fed into a polymerization reactor and that is activated to an active polymerization catalyst within the polymerization reactor by an additional component, a cocatalyst, such as an aluminum alkyl cocatalyst.

The terms “precursor” and “catalyst precursor” as used herein mean a portion of the catalyst composition containing the transition metals that is subjected to an additional reaction step to convert it into a procatalyst.

The term “virgin granular polymer” means a granular polyolefin polymer exiting a polymerization reactor with no further processing, such as grinding, pelletizing, extruding or the like.

The term “granular polymer” means a polymer produced in a fluidized bed or slurry polymerization reactor and which exits the reactor in a granular or particle form.

The term “mean” means an unweighted average.

The instant invention is a virgin granular polymer, a reaction product, articles made therefrom, and methods for making such articles.

The polymer according to a first aspect of the present invention is a virgin granular polymer comprising polymer particles wherein at least 90% by weight of the granular polymer particles have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1, and further wherein the virgin granular polymer has an I_{21} less than or equal to 30. All individual values and subranges from greater than 90% by weight are included herein and disclosed herein; for example, the weight percent of the granular polymer particles having the ascribed characteristics may be from a lower limit of 90, 91, 92, 93, or 94 weight percent to an upper limit of 91, 92, 93, 94, 95, 96, 97, 98, 99 or 100 weight percent, based on the total weight of the virgin granular polymer. For example, the weight percent of the granular polymer particles having the ascribed characteristics may be in the range of from 90 to 95 weight percent, or in the alternative from 91 to 98 weight percent, or in the alternative, from 95 to 99 weight percent, or in the alternative from 93 to 99 weight percent, or in the alternative, from 94 to 97 weight percent, based on the total weight of the virgin granular polymer.

Further, the at least 90% by weight of the granular polymer particles have an I_{21} wherein the ratio of the standard deviation of I_{21} to the mean of the I_{21} of the granular polymer is less than 0.2. All individual values from less than 0.2 are included herein and disclosed herein; for example, the ratio of the standard deviation of I_{21} to the mean of the I_{21} of the granular polymer may be from an upper limit of 0.02. 0.04, 0.06, 0.08, 0.1, 0.13, 0.15, 0.17, 0.19 or 0.2.

Further, the at least 90% by weight of the granular polymer particles have an I_{21} and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1. All individual values from less than 0.1 are included herein and disclosed herein; for example, the ratio of the standard error of a linear fit to the mean of the granular polymer may be from an upper limit of 0.02, 0.04, 0.06, 0.08, or 0.1.

Further, the at least 90% by weight of the granular polymer particles have an I_{21} less than or equal to 70. All individual values of less than or equal to 70 are included herein and disclosed herein; for example, I_{21} may be less than or equal to 70, or in the alternative less than or equal to 50, or in the alternative less than or equal to 40, or in the alternative less than or equal to 30, or in the alternative less than or equal to 20, or in the alternative less than or equal to 10, or in the alternative less than or equal to 8, or in the alternative less than or equal to 4.

In one embodiment, the virgin granular polymer is a polyethylene.

In a further embodiment, the virgin granular polymer is a polyethylene produced in a gas phase or slurry polymerization process.

The polymer according to a second aspect of the present invention is a virgin granular polymer comprising polymer particles wherein at least 90% by weight of the granular polymer particles a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001, and further wherein the virgin granular polymer has an I_{21} less than or equal to 70. All individual values and subranges from greater than 90% by weight are included herein and disclosed herein; for example, the weight percent of the granular polymer particles having the ascribed characteristics may be from a lower limit of 90, 91, 92, 93, or 94 weight percent to an upper limit of 91, 92, 93, 94, 95, 96, 97, 98, 99 or 100 weight percent, based on the total weight of the virgin granular polymer. For example, the weight percent of the granular polymer particles having the ascribed characteristics may be in the range of from 90 to 95 weight percent, or in the alternative from 91 to 98 weight percent, or in the alternative, from 95 to 99 weight percent, or in the alternative from 93 to 99 weight percent, or in the alternative, from 94 to 97 weight percent, based on the total weight of the virgin granular polymer.

Further, the at least 90% by weight of the granular polymer particles have a density wherein the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002. All individual values from less than 0.002 are included herein and disclosed herein; for example, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer may be from an upper limit of 0.0002. 0.0004, 0.0006, 0.0008, 0.001, 0.0013, 0.0015, 0.0017, 0.0019 or 0.002.

Further, the at least 90% by weight of the granular polymer particles have a density and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001. All individual values from less than 0.001 are included herein and disclosed herein; for example, the ratio of the standard error of a linear fit to the mean of the density may be from an upper limit of 0.0002, 0.0004, 0.0006, 0.0008, or 0.001.

Further, the at least 90% by weight of the granular polymer particles have an I_{21} less than or equal to 70. All individual values of less than or equal to 70 are included herein and disclosed herein; for example, I_{21} may be less than or equal to 70, or in the alternative less than or equal to 60, or in the alternative less than or equal to 50, or in the alternative less than or equal to 40, or in the alternative less than or equal to 30, or in the alternative less than or equal to 10, or in the alternative less than or equal to 8, or in the alternative less than or equal to 4.

The polymer according to a third aspect of the present invention is a reaction product of polymerizing at least one olefin monomer in the presence of: (A) at least one catalyst precursor produced by contacting a Group 4 metal compound with one or more Titanium compounds selected from the group of $TiCl_3$ (Al-activated or hydrogen-reduced), and $Ti(OR)_4$ where R is ethyl, isopropyl or n-butyl in the presence of an alcohol solution comprising at least one C_2-C_4 alcohol and at least one of $MgCl_2$ and magnesium compounds which form $MgCl_2$ in the presence of the alcohol solution to form a catalyst precursor solution, forming said catalyst precursor solution into solid particles and subsequently halogenating the solid particles; and (B) at least one co-catalyst; wherein the reaction product comprises a granular polymer comprised of polymer particles and further wherein at least 90% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1. All individual values and subranges from greater than 90% by weight of the granular polymer particles are included herein and disclosed herein; for example, the weight percent of the granular polymer particles having the ascribed characteristics may be from a lower limit of 90, 91, 92, 93, or 94 weight percent to an upper limit of 91, 92, 93, 94, 95, 96, 97, 98, 99 or 100 weight percent, based on the total weight of the granular polymer. For example, the weight percent of the granular polymer particles having the ascribed characteristics may be in the range of from 90 to 95 weight percent, or in the alternative from 91 to 98 weight percent, or in the alternative, from 95 to 99 weight percent, or in the alternative from 93 to 99 weight percent, or in the alternative, from 94 to 97 weight percent, based on the total weight of the granular polymer.

The polymer according to a fourth aspect of the present invention is a reaction product of polymerizing at least one monomer, in the gas phase, in the presence of: (A) at least one catalyst precursor produced by contacting a Group 4 metal compound with one or more Titanium compounds selected from the group of $TiCl_3$ (Al-activated or hydrogen-reduced), and $Ti(OR)_4$ where R is ethyl, isopropyl or n-butyl in the presence of an alcohol solution comprising at least one C_2-C_4 alcohol and at least one of $MgCl_2$ and magnesium compounds which form $MgCl_2$ in the presence of the alcohol solution to form a catalyst precursor solution, forming said catalyst precursor solution into solid particles and subsequently halogenating the solid particles; and (B) at least one co-catalyst; wherein the reaction product comprises a granular polymer comprised of polymer particles and further wherein at least 90% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001. All individual values and subranges from greater than 90% by weight of the granular polymer particles are included herein and disclosed herein; for example, the weight percent of the granular polymer particles having the ascribed characteristics may be from a lower limit of 90, 91, 92, 93, or 94 weight percent to an upper limit of 91, 92, 93, 94, 95, 96, 97, 98, 99 or 100 weight percent, based on the total weight of the granular polymer. For example, the weight percent of the granular polymer particles having the ascribed characteristics may be in the range of from 90 to 95 weight percent, or in the alternative from 91 to 98 weight percent, or in the alternative, from 95 to 99 weight percent, or in the alternative from 93 to 99 weight percent, or in the alternative, from 94 to 97 weight percent, based on the total weight of the granular polymer.

In one embodiment, the inventive virgin granular polymer is a combination of two or more of the embodiments described herein.

In one embodiment, the reaction product is a combination f tow or more of the embodiments described herein.

Catalyst precursors useful in the invention include those with no internal electron donors. The catalyst precursors may comprise substantially spheroidal shaped particles of a magnesium halide containing precursor, the particles having an average size (D50) of from 10 to 70 microns, from 15 to 50 microns, or from 20 to 35 microns, having been produced via spray drying from a nominally neutral acidity feedstock. The catalyst precursor may be produced by: a) providing a liquid composition comprising i) a magnesium halide compound or magnesium compound that is convertible to magnesium halide via halogenation, ii) an alcoholic solvent or diluent, iii) at least two transition metal compounds wherein the transition metals are selected from the metals of Groups 3-10 and of the Periodic Table of the Elements and wherein one of the metals is Titanium and the other metal is Zirconium or Hafnium or both, iv) optionally a filler wherein the acidity of the liquid composition is adjusted to essentially neutral by adjusting the composition of either the Titanium compound or the magnesium compound that is convertible to magnesium chloride; b) spray-drying the composition in a closed cycle spray drier to form a spray-dried particle; and c) collecting the resulting solid particles which are a precursor powder. Representative magnesium compounds that convert to $MgCl_2$ in the presence of the alcohol solution include magnesium alkoxides and magnesium alkyl carbonates.

The spray-dried procatalyst particles may be combined with a cocatalyst to form an active catalyst composition. The activation may occur prior to or simultaneously with, or after contacting with the monomer or monomers to be polymerized. In some embodiments of the present invention, the procatalyst is partially or fully activated outside the polymerization reactor by contacting the procatalyst with a portion of the cocatalyst in an inert liquid hydrocarbon as disclosed in U.S. Patent Nos. 6,187,866 and 6,617,405, the disclosures of which are incorporated herein by reference. After contacting the procatalyst composition with the cocatalyst, the hydrocarbon solvent may be removed by drying or, preferably, the catalyst composition may be directly fed to the polymerization reactor where the activation is completed with additional amounts of the same or a different cocatalyst.

Additional precursor, procatalysts and catalysts useful in the preparing the inventive virgin granular polymers are described in copending application U.S. Application Serial No. 12/759,515 filed on April 13, 2010, the disclosure of which is incorporated herein by reference.

The virgin granular polymers of the present invention are useful in a variety of applications ranging from blow molding products to stretch tapes. The inventive virgin granular polymers are useful in direct applications such as rotomolding, blowmolding or sheet formation and are particularly amenable to the production of very high molecular weight polymers that may be very difficult to pelletize for homogeneity, i.e. polymers with high load melt indices (I_{21}) in the 0.1 to 3 range.

The inventive virgin granular polymers may be produced in existing fluidized bed or slurry reaction systems, and may be produced using single or multiple reactor systems. The inventive virgin granular polymers may be produced, for example, in the reactor systems disclosed in WO2008US87581 and WO2008US87378, the disclosures of which are incorporated herein by reference

Variation in the inventive virgin granular polymer properties are controlled within the limits prescribed by measurement method precision. Resin Density, for example, may be precisely measured according to ASTM D792. Table 1 provides the Standard Deviation (SD) and *r* value of resin density measurements taken according to ASTM D792 on a test high density polyethylene.

Table 1

Method	**Standard Deviation (SD) of multiple tests within one laboratory**	***r* value =2.8*SD**
ASTM D792	0.0008	0.0022

ASTM D792 defines the repeatability or repeatability index, r, as: $r = 2.8 \bullet (SD)$. A measurement on a material has repeatability if two test results obtained within one laboratory differ by the *r* value or less for that material. The *r* value is the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory. Thus, all particle size fractions of the inventive virgin granular polymer should have a density within ±0.0022 g/cc of each other. In such instance, the virgin granular polymer can be said to an equivalent density across all polymer particle fractions.

In like manner, for I_{21}, I_5 and I_2 there are known levels of variation that are the result of the test itself independent of the actual normal variation that may occur in any continuous process. Again, to provide for the optimum granular resin performance, it is desired that >90% by weight and preferably >95% by weight of the granular resin has melt flow properties that are within this known level of variation in measurement.

In particular, for very high molecular weight polymers, the I_{21} value is generally measured using ASTM standard 1238 D, Procedure A (cut-off). Repeatability indices are not given for I_{21}, only for I_2, however one of ordinary skill in the art would anticipate that the repeatability for I_{21} would be similar to that for I_2. Table 2 below provides the repeatability, r, (i.e., precision) indices for I_2 as specified in ASTM 1238D, Procedure A, wherein Standard Deviation = SD.

Table 2

Material/ Condition	**Mean I_2 (g/10 min)**	**SD between Labs**	**Repeatability =2.83*SD**	**% of Value***	**Low I_2 (g/10 min) Value**	**High I_2 (g/10 min) Value**
Polyethylene 190/2.16	0.27	0.022	0.062	23.1	0.208	0.332
Polyethylene 190/2.16	0.4	0.038	0.108	26.9	0.292	0.508
Polyethylene 190/2.16	2.04	0.079	0.224	11.0	1.816	2.264

* Calculated as r value divided by average I_2 multiplied by 100.

Because the actual measured quantity, (grams/10 minutes (g/10 min)) flowing through a die of a prescribed size at a prescribed temperature is not fully representative of the actual molecular weight of the polymer, the natural logarithm ("ln" herein) of the I_{21}, I_5 or I_2 is used as this is a better predictor of actual molecular weight of the polymer. In general, the change in $\ln(I_{21})$ is representative of the change in number average molecular weight whereas the change in $\ln(I_2)$ is representative of the change in weight average molecular weight.

Examples

The following examples illustrate the present invention but are not intended to limit the scope of the invention.

Inventive Examples: Precursor and Procatalyst Preparation

The catalyst precursor solution used in each of the polymerization process, Inventive Examples 1-4 below, was prepared as follows:

Under inert reaction conditions, the components shown in Table 3 were charged to a solution preparation vessel.

Table 3

Feedstock Charge	
Ethanol, kg	1000
$MgCl_2$, kg	50.34
$TiCl_3$ AA, kg	20.34
$HfCl_4$, kg	33.64
CAB-O-SIL™ TS-610, kg	70.00

The ethanol was charged first followed by $MgCl_2$, $HfCl_4$ and $TiCl_3$ (AA). Amounts listed were aim values, some slight losses occurred although the amounts given in Table 1 are all within 5% by weight of the amount actually added. The ethanol used was specially denatured ethanol from BrüggemannChemical U.S., Inc. (Newtown Square, PA) containing about 0.5% by weight of toluene and <100 ppm water. Magnesium chloride was obtained from SRC, Inc. (Cleveland, OH), Hafnium Tetrachloride (containing up to 1 wt% Zirconium) from ATI Wah-Chang (Albany, Oregon) and aluminum activated titanium trichloride from W.R. Grace & Co. CAB-O-SIL™ TS-610 (which is a filler) was obtained from the Cabot Corporation.

The mixture was stirred at 35 to 50 °C under a nitrogen blanket for about 8 hours prior to the start of spray drying. The spray drying process produced a catalyst precursor powder. A 2.5 meter Gea Niro Rotary Atomizer Type FS-15 atomizer wheel (available from Gea Niro, Søborg, Denmark) was used. Atomizer speed was adjusted to obtain an average particle size of the catalyst precursor of about 30 microns. Inlet temperature was adjusted to achieve an outlet temperature between 105 and 110 °C and the feedstock was spray dried at a rate of 100 to 150 kg/hr.

Particle size distribution in the catalyst precursor powder was determined using a Malvern Mastersizer 2000 particle size analyzer with heptane as the dispersant. The General Purpose (Spherical) particle model was used to calculate particle size. Sonication was utilized (50% power, 30 to 60 seconds) to break up any agglomerates that might have formed in the sampling process. Table 4 lists the particle size distribution of the catalyst precursor powder by percent by volume.

Table 4

Particle Size, Microns	Volume %	Particle Size, Microns	Volume %
0.55	0.07	8.71	3.07
0.63	0.1	10	3.02
0.724	0.12	11.482	2.91
0.832	0.15	22.909	4.63
0.955	0.18	26.203	5.58
1.096	0.21	30.2	6.52
1.259	0.23	34.674	7.26
1.445	0.24	39.811	7.64
1.66	0.22	45.709	7.52
1.905	0.21	52.481	6.88
2.188	0.23	60.256	5.8
2.512	0.3	69.183	4.45
2.884	0.45	79.433	3.03
3.311	0.7	91.201	1.75
3.802	1.05	104.713	0.73
4.365	1.49	120.226	0.11
5.012	1.95		
5.754	2.4		
6.607	2.76		
7.586	2.99		

The catalyst precursor powder was then dispersed in isopentane to form a catalyst precursor powder solution. The halogenation agent, ethylaluminum sesquichloride (EASC), was then added to the catalyst precursor powder solution at a 2.0 “Cl to ethoxide” molar ratio to form a procatalyst slurry. Ethoxide as used herein means free ethanol remaining in the spray dried catalyst precursor and ethoxide ligands present, for example, on the Hf, Ti and/or Zr components. Ethoxide content is measured as ethanol after the catalyst precursor is contacted with acidified water (i.e., HCl added to obtain a pH of about 1). A sample of the liquid phase was then injected into a gas chromatograph and ethanol content determined. The precursor prior to halogenation had an average ethoxide content of about 25 wt% (ranging from 24 to 27 wt% in a number of measurements).

The precursor slurry was then mixed at 50 °C for one hour, and the solids then allowed to settle. The supernatant liquid was decanted, an additional volume of isopentane was added, and this washing step was repeated two additional times.

HYDROBRITE 380 mineral oil (available from Sonneborn, LLC, Mahwah, NJ) was then added to the solids remaining following the washing process to produce a slurry of procatalyst. Vacuum was drawn on the procatalyst slurry for approximately one hour to evaporate any isopentane remaining following the washing process.

The catalyst precursor for use in the polymerization process, Inventive Example 5 below, was prepared in the same manner as that described above for preparation of the precursor for use in Inventive Examples 1 - 4 with the following exceptions:
Feedstock: Titanium tetraisopropylate was used at the same molar ratio to Magnesium and Hafnium instead of the Titanium Trichloride.

Spray Drying: The spray dryer was a Gea Niro MOBILE MINOR spray dryer (available from Gea Niro, Søborg, Denmark) using the vaned atomizer wheel. Atomizer speed was adjusted to obtain particles having a D50 of about 25 microns and was approximately 34,000 RPM.

Feedrate: Feedrate was adjusted to maintain a 105 to 110°C outlet temperature. Average feed rate was ~100 grams/hour.

Particle size distribution: A narrower particle size distribution was obtained. Particle Size was measured using an LA-950 particle size analyzer (which utilizes software containing both ISO 13320 and USP 429 calculation) available from Horiba Ltd with heptane as the diluent.

Table 5 provides the particle size distribution by volume percent for the catalyst precursor powder for Inventive Example 5.

Table 5

Size Microns	Volume %	Size Microns	Volume %
4.472	0	34.255	10.821
5.122	0	39.234	8.355
5.867	0.124	44.938	5.855
6.72	0.22	51.471	3.91
7.697	0.386	58.953	2.547
8.816	0.665	67.523	1.648
10.097	1.118	77.339	1.03
11.565	1.854	88.583	0.642
13.246	2.977	101.46	0.412
15.172	4.578	116.21	0.274
17.377	6.655	133.1	0.2
19.904	9.007	152.45	0.159
22.797	11.169	174.6	0.136
26.111	12.478	200	0.126
29.907	12.378	229	0.131
		262.4	0.144

The catalyst precursor ethoxide content was about 25 wt%. The catalyst precursor for Inventive Example 5 was converted into a procatalyst using the same procedure as that used to prepare the procatalysts used for Inventive Examples 1-4.

Polymerization Processes and Polymers – Inventive Examples 1-5

For Inventive Example 1 the polymerization reaction was effected in the first reactor of the dual reactor system as described in WO2008US87581 and WO2008US87378, the disclosures of which are incorporated herein by reference. That is, the product of the first reactor was not further subjected to polymerization in a second reactor. Table 6 below provides the reactor conditions and the properties of the polymer produced for Inventive Example 1.

Table 6

REACTOR CONDITIONS	
Temperature, °C	82.0
H_2/ C_2 ratio	0.1416
C_6/ C_2 ratio	0.0131
C_2 partial pressure, PSIG	55.0
Calculated Production Rate, lbs/hr	36.4
Bed Weight, lbs	82.4
Static Volts 90 min average	23.0
Static Range 90 average	77.3
Cocatalyst type	Triethylaluminum (TEAL)
Continuity Additive (CA), ppm in bed	10
Isopentane, mole%	18.5
delta dew point	5.6
Residence Time, hours	2.27
POLYMER PROPERTIES	
I_{21}, dg/min	1.120
Density, g/cc	0.9377
Average Particle Size, inch	0.029
Bulk Density, lb/ft^3	25.900
Ti ppmw	3.95
Al ppmw	28.92

A representative sample of the bulk polymer was fractionated using a standard geometric sieve set (10/18/35/60/120/200 - followed by pan) with openings in the sieve set of 2000 /1000/500/250/125/70 microns, respectively. The residual aluminum content in the fractions was determined via X-Ray Fluorescence (XRF) using appropriate standards. The residual aluminum content was essentially constant across all polymer particle sizes, as detailed in Table 7 below, which provides the analysis for two separate samples of Inventive Example 1.

Table 7

Polymer Particle Size (micron)	**Sample 1 of Inventive Example 1, Wt %**	**Average Al by XRF, Sample 1**	**Sample 2 of Inventive Example 1, Wt %**	**Average Al by XRF, Sample 2**
Example 1				
2000	3.6287	29	30	29.5
1000	36.6802	28	27	27.5
500	28.4707	25	26	25.5
250	18.7506	29	30	29.5
125	8.4994	35	35	35
70	2.2401			
less than 70	1.7396			
Blended Sample		31	32	31.5

For Inventive Example 2, the polymerization was performed in linked reactors to produce a very broad molecular weight distribution polymer. Table 8 below provides the reactor conditions and the properties of the polymer produced for Inventive Example 2. The first reactor product was fractionated as described above in connection with Inventive Example 1, and the results are given in Table 9.

Table 8

REACTOR PROPERTIES	
Temperature, °C	82.0
H_2/ C_2 ratio	0.1000
C_6/ C_2 ratio	0.0181
C_2 partial pressure, PSIG	42.4
Calculated Production Rate, lbs/hr	30.0
Bed Weight, lbs	150.5
Static Volts 90 min average	-63.2
Static Range 90 average	317.3
Cocatalyst type	TEAL
Continuity Additive, ppm in bed	12
Isopentane, mol%	18.1
delta dew point	7.0
Residence Time, hours	5.02
POLYMER PROPERTIES	
Al, ppmw	42.39
I_{21}, dg/min	0.937
Density, g/cc	0.9353
Average Particle Size, inch	0.035
Bulk Density, lb/ft^3	24.100
Ti, ppmw	3.89

Table 9

Particle Size (micron)	wt% on Screen	Density (g/cc) *	Density Delta	ln I_{21}	I_{21} (dg/min) *	Al (ppm) **	Al Variation ***
Inventive Example 2	Bulk	0.9351		-0.07	0.937	66.5	
2000	3.83	0.9352	-0.0001	0.28	1.321	72.5	0.090226
1000	25.28	0.9340	0.0011	0.00	1.000	61	-0.08271
500	26.92	0.9338	0.0013	0.00	1.002	82	0.233083
250	22.77	0.9355	-0.0004	-0.13	0.880	65	-0.02256
125	15.73	0.9368	-0.0017	-0.30	0.738	60.5	-0.09023
70	3.68	nd****			nd	nd	
less than 70	1.79	Nd			nd	nd	

*Extruded or Pellets

**Average of two measurements

***(measured average)/average

****"nd" means not detected.

The density and I_{21} values were all within the repeatability limits of the method or the standard deviation of the mean.

For Inventive Example 3, the polymerization was conducted in a dual reactor system as described in WO2008US87581 and WO2008US87378. Table 10 below provides the reactor conditions for both the first and second reactors for Inventive Example 3. Table 11 lists the properties of the polymer produced in the first reactor. Table 12 lists the properties of the polymer produced in the second reactor. The second reactor polymer product was fractionated as described above in connection with Inventive Example 1, and the results are given in Table 13.

Table 10

1ST REACTOR CONDITIONS		2ND REACTOR CONDITIONS	
Temperature, °C	82.0	Temperature, °C	110.0
H_2/ C_2 ratio	0.1187	H_2/ C_2 ratio	0.601
C_6/ C_2 ratio	0.0065	C_6/ C_2 ratio	0.0004
C_2 partial pressure, PSIG	70.7	C_2 partial pressure, PSIG	93.3
Calculated Production Rate, lbs/hr	33.6	Calculated Production Rate, lbs/hr	21.5
Inlet Dew Point, °C	68.6	Split by Ti Analysis	0.688
Bed Weight, lbs	78.5	Energy Balance Rate lb/hr	21.3
Cocatalyst type	TEAL	Energy Balance Rate	55.1
Continuity Additive, ppm in bed	10.5	Mass Balance Hourly rate	52.2
Isopentane mol%	18.1	Bed Weight, lbs	129.5
Residence Time, hours	2.34	Residence Time, hours	2.35

Table 11

FIRST REACTOR POLYMER PROPERTIES	
I_{21}, dg/min	0.648
Density, g/cc	0.9409
Average Particle Size, inch	0.043
Fines, wt%	1.630
Bulk Density, lb/ft^3	25.100
Residual Ti, ppmw	2.11
Residual Al, ppmw	23.32

Table 12

SECOND REACTOR POLYMER PROPERTIES	
I_{21}/I_2	85.76923
I_2, dg/min	0.0793
I_{21}, dg/min	6.8056
I_5, dg/min	0.3601
I_{21}/I_5	18.9
Density, g/cc	0.9534
Bulk Density, lb/ft^3	28.4005
Average Particle Size, inch	0.0436
Fines, wt%	1.6694
Residual Al, ppmw	21.9733
Residual Ti, ppmw	1.4496
Al/Ti ratio	26.91

Table 13

Particle Size (micron)	**wt%**	**Density (g/cc)**	**Density Delta**	**Absolute Value Difference**	**ln I_2**	**I_2, dg/min**	**ln (I_5)**	**I_5, dg/min**
Inventive Example 3	Bulk	0.9538			-2.50	0.082	-1.02	0.36
2000	8.77	0.9521	0.0017	0.0017	-2.32	0.099	-0.86	0.42
1000	36.88	0.9537	.0001	.0001	-2.58	0.076	-1.03	0.36
500	25.51	0.9541	-0.0003	0.0003	-2.33	0.098	-0.87	0.42
250	19.56	0.9551	-0.0013	0.0013	-2.26	0.104	-0.78	0.46
125	8.17	0.9541	-0.0003	0.0003	-2.42	0.089	-0.97	0.38
Particle Size (micron)	wt%	ln (I_{21})	I_{21}, dg/min	Al ppm				
Example 3	Whole	1.95	7.01	20.5				
2000	8.77	2.05	7.79	26				
1000	36.88	1.91	6.74	23				
500	25.51	2.10	8.18	22.5				
250	19.56	2.09	8.12	21.5				
125	8.17	1.95	7.02	21.5				
70	0.50	nd						
less than 70	0.61	nd						

Samples of the polymer of Inventive Example 3 were converted into pellets in a KOBE™ LCM-100 twin screw extruder and then converted into inflation films, as is generally known in the art. More specifically, the inflation film is formed by extruding the polymer resin at a temperature within the range of from 180 to 220 °C., for example, and subsequently causing the extruded sheet, by means of a proper form of air, to be simultaneously cooled and inflated to a prescribed size. The film appearance rating was good indicating the substantial absence of gels.

For Inventive Example 4, the polymerization was conducted as described for Inventive Example 1 except that the conditions of the sole reactor were at the values set out in Table 14. The polymer product was fractionated as described above in connection with Inventive Example 1, and the results are given in Table 15.

Table 14

Temperature, °C	82.00
C_2 partial pressure, PSIG	71.8918
C_6/ C_2 ratio	0.0145
H_2/ C_2 ratio	0.1050
Residence Time, hours	~3.5
Isopentane, mol %	16.61
Bulk Density, lb/ft^3	22.80
Average Particle Size, inch	0.047

Table 15

Particle Size Microns	Wt%	Density (g/cc)	Density Delta	ln(I_{21})	I_{21}, dg/min
Bulk Sample		0.9369		-0.29	0.751
2000	9.330	0.9357	0.0012	-0.02	0.983
1000	50.110	0.9366	0.0003	-0.14	0.867
500	24.250	0.9366	0.0003	-0.10	0.906
250	11.660	0.937	-0.0001	-0.17	0.846
125	4.030	0.9375	-0.0006	-0.33	0.722
70	0.450	nd			nd
less than 70	0.170	nd			nd

As can be seen in Table 15, greater than 95% of the resin particles have the same physical properties.

Comparative Example 1 – Catalyst Precursor and Procatalyst Preparation, Polymerization and Polymer

Comparative Example Procatalyst 1 was prepared following the examples of U.S. Patent No. 6,187,866, except as expressly described. The disclosure of U.S. Patent No. 6,187,866 is incorporated herein by reference. A feedstock primarily containing anhydrous tetrahydrofuran (THF), dried to less than about 50 ppm water, was heated to approximately 50 °C. Granular magnesium metal (100 to about 4000 micron in particle size) was then added to the THF followed by addition of titanium tetrachloride. The mixture was then heated to approximately70 °C. Without being bound by any particular theory, it is currently believed that the Mg metal chemically reduces the titanium tetrachloride to lower valence states, primarily to the +3 valence state. An Mg/Ti molar ratio of slightly higher than 0.5 was used to assure essentially complete reduction of the Ti^{+4} to lower valence states. Magnesium dichloride was then added to bring the total molar ratio of Magnesium to Titanium in the mixture to between 5.5:1 and 6:1. This mixture was then heated and mixed further for approximately 4 to 6 hours followed by filtration to remove any unreacted magnesium metal and impurities present in the magnesium dichloride that were insoluble in the THF. Finally, fumed silica, CAB-O-SIL™ TS-610, was added and mixing was continued until the fumed silica was dispersed, producing a spray drying feedstock. Per 100 liters of THF, 4.8 to 5 moles of Magnesium metal, 9.7 to 10.1 moles of titanium tetrachloride and 49 to 55 moles of magnesium dichloride were used to make the solution. Approximately 6.2 to 7 kilograms of the fumed silica were added to produce the spray drying feedstock. The spray drying feedstock was spray dried using a Niro Atomizer 8-foot diameter closed cycle spray dryer equipped with an FS-15 rotary atomizer using nitrogen as the drying gas. The rotary atomizer was adjusted to give catalyst particles with a D50 of 18 microns. The spray dried catalyst precursor contained approximately 2.5 weight percent Ti, 6.3 weight percent Mg, and 25 to 29 weight percent THF. The spray dried catalyst precursor particles had a D50 of 25 microns and a span [(D90-D10)÷D50] of less than 2 as determined by means of a Leeds and Northrup MICROTRAC™ particle size analyzer using a dodecane solvent. The catalyst precursor particles were mixed with mineral oil under a nitrogen atmosphere to form a slurry containing approximately 28 weight percent of the solid catalyst precursor. The catalyst precursor slurry was then fed to the polymerization reactor. Triethyaluminum was used as cocatalyst.

For Comparative Example 1, the polymerization was conducted in a dual reactor system according to example 1 of U.S. Patent No. 7,714,072, with the exception that the catalyst precursor was not pre-contacted with aluminum alkyl prior to introduction into the reactor. The disclosure of U.S. Patent No. 7,714,072 is incorporated herein by reference. The resulting granular resin was sieved using the sieve set described in connection with Inventive Example 1 and the key resin melt flow properties were measured. Table 16 lists the conditions of both first and second reactors and the properties of the polymers produced in each reactor.

Table 16

FIRST REACTOR CONDITIONS		**SECOND REACTOR CONDITIONS**	
Temperature, °C	85	Temperature, °C	110.0
H_2/ C_2 ratio	0.023 to 0.026	H_2/ C_2 ratio	1.55 to 1.65
C_6/ C_2 ratio	0.03 to 0.035	C_6/ C_2 ratio	0.010
C_2 partial pressure, PSI	32 to 38	C_2 partial pressure, PSI	75 to 80
Cocatalyst type	TEAL	Split	~0.6
Residence Time, hours	2.3 to 2.4	Residence Time, hours	2 to 2.2
FIRST REACTOR POLYMER PROPERTIES		**SECOND REACTOR POLYMER PROPERTIES**	
I_{21}, dg/min	0.5	I_{21}, dg/min	11 to 12
Density, g/cc	0.930 to 0.932	I_2, dg/min	0.1 to 0.12
Average Particle Size (APS), inch	0.027 to 0.030	Density, g/cc	0.9534
Fines wt %	4 to 5	Bulk Density lb/ft^3	23 to 24
Bulk Density lb/ft^3	20 to 21	APS, inch	0.028 to 0.030
Ti ppm	4..5 to 5	Fines wt %	3.5 to 4
Al/Ti ratio	35 to 40	Al/Ti	50 to 60
		Ti ppm	2.8 to 3.0

A sample of the polymer produced in the second reactor for Comparative Example 1 was examined for polymer particle size distribution as described in connection with Inventive Example 1. The particle size distribution is shown in Table 17. Table 17 further includes flow properties for each of the fractions obtained in the sieving process.

Table 17

Avg. Size µm	**% In Band**	**Cumulative %**	**I_2, dg/min**	**I_{21}, dg/min**	**I_{21}/I_2**
88	2.73	2.73	0.1540	28.5	185.1
115	5.38	8.11	0.1610	21.4	132.9
162	12.44	20.55	0.1280	15.8	123.4
229	4.64	25.19	0.1380	15.5	112.3
354	33.08	58.27	0.1190	13.7	115.1
595	21.82	80.09	0.0928	11.4	122.8
771	11.15	91.24	0.0556	6.89	123.9
917	4.80	96.04		5.14	
1414	3.93	99.97		3.52	
3070	0.03	100.00			
Bulk Polymer			**0.1020**	**11.5**	**113**

For Comparative Example 2, the polymerization reaction was carried out as described for Comparative Example 1 except that the reaction conditions were adjusted to increase the overall residence time in each of the reactors. Table 18 lists the conditions for both the first and second reactors for Comparative Example 2.

Table 18

FIRST REACTOR CONDITIONS		**SECOND REACTOR CONDITIONS**	
Temperature, °C	85	Temperature, °C	110.0
H_2/ C_2 ratio	0.023 to 0.026	H_2/ C_2 ratio	1.6 to 1.65
C_6/ C_2 ratio	0.03 to 0.032	C_6/ C_2 ratio	0.010
C_2 partial pressure, PSI	40 to 42	C_2 partial pressure, PSI	70 to 75
Cocatalyst type	TEAL	Split	~0.6
Residence Time, hour	2.6 to 2.8	Residence Time, hour	2.8 to 3
FIRST REACTOR POLYMER PROPERTIES		**SECOND REACTOR POLYMER PROPERTIES**	
I_{21}, dg/min	0.4 to 0.5	I_{21}, dg/min	11 to 12
Density, g/cc	0.930 to 0.932	Density, g/cc	0.946 to 0.948
APS, inch	0.025 to 0.027	APS, inch	0.026 to 0.028
Bulk Density lb/ft^3	20 to 21	Bulk Density lb/ft^3	23 to 24
Fines wt %	4 to 5	Fines wt %	5 to 6
Al/Ti ratio	35 to 40	Al/Ti ratio	50 to 60
Ti ppmw	4.5 to 5	Ti ppmw	2.8 to 3
		I_2, dg/min	0.09 to .1

A sample of the polymer produced Comparative Example 2 in the second reactor was examined for polymer particle size distribution as described in connection with Inventive Example 1. The particle size distribution for Comparative Example 2 is shown in Table 19. Table 19 further includes flow properties for each of the fractions obtained in the sieving process.

Table 19

Avg. Size, µm	% in Band	% Cumulative	I_2, dg/min	I_{21}, dg/min	I_{21}/I_2
88	2.14	2.14	0.1542	23.9	155.0
115	4.69	6.83	0.1432	14.0	97.8
162	11.54	18.37	0.1096	13.8	125.9
229	4.40	22.77	0.1082	13.1	121.1
354	31.79	54.56	0.0898	10.1	112.5
595	23.52	78.08	0.0564	8.64	153.2
771	12.18	90.26		5.63	
917	5.28	95.54		3.86	
1414	4.43	99.97			
3070	0.03	100.00			
Bulk Sample			0.0942	9.49	101

For Comparative Example 3, the polymerization reaction was as described for Comparative Example 1 except that the reaction conditions were adjusted to lower the overall residence time in each of the two reactors. Table 20 lists the conditions for both the first and second reactors for Comparative Example 3.

Table 20

FIRST REACTOR CONDITIONS		**SECOND REACTOR CONDITIONS**	
Temperature, °C	85	Temperature, °C	110.0
H_2/ C_2 ratio	0.023 to 0.026	H_2/ C_2 ratio	1.65 to 1.75
C_6/ C_2 ratio	0.03 to 0.035	C_6/ C_2 ratio	0.002
C_2 partial pressure, PSI	40 to 44	C_2 partial pressure, PSI	80 to 85
Cocatalyst type	TEAL	Split	~0.6
Residence Time, hr	1.6 to 1.8	Residence Time, hr	1 to 1.2
FIRST REACTOR POLYMER PROPERTIES		**SECOND REACTOR POLYMER PROPERTIES**	
I_{21}, dg/min	0.4 to 0.5	I_{21}, dg/min	11 to 12
Density, g/cc	0.928 to 0.930	Density, g/cc	0.946 to 0.948
APS, inch	0.025 to 0.027	Bulk Density, lb/ft^3	23 to 24
Fines wt %	4 to 5	APS, inch	0.026 to 0.028
Bulk Density, lb/ft^3	25.100	Fines wt %	5 to 6
Ti ppmw	3..5 to4	Al/Ti ratio	50 to 60
Al/TI ratio	35 to 40	Ti ppmw	2.2 to 2.4
		I_2, dg/min	0.09 to .1

A sample of the polymer produced Comparative Example 3 in the second reactor was examined for polymer particle size distribution as described in connection with Inventive Example 1. The particle size distribution for Comparative Example 3 is shown in Table 21. Table 21 further includes flow properties for each of the fractions obtained in the sieving process.

Table 21

Avg. Size, µm	% in Band	% Cumulative	I_2, dg/min	I_{21}, dg/min	I_{21}/I_2
88	2.75	2.75	0.1196	25.8	215.7
115	4.81	7.56	0.1032	21.4	207.4
162	12.28	19.84	0.0972	16.0	164.6
229	4.49	24.33	0.0992	12.1	122.0
354	31.58	55.91	0.1088	12.4	114.0
595	23.31	79.22	0.0676	9.47	140.1
771	11.98	91.20	0.0462	6.26	135.5
917	4.68	95.88		4.85	
1414	4.05	99.93		3.9	
3070	0.07	100.00			
Bulk Sample			0.0948	10.1	107

As can be seen in Tables 19 and 21, neither of Comparative Examples 2 or 3 provided an improvement in the granular heterogeneity or in the final polymer. For each of the polymers produced in Comparative Examples 2 and 3, polymer samples were converted into pellets using an LCM-100 extruder with a 100 mesh screen pack (i.e. the melt passed through a 100 mesh screen). The pellets were then converted into inflation films and the appearance of the films judged visually based on standards that range from +50 which equates to a substantial absence of any imperfections in the film to -50 which equates to an extremely poor looking film with multiple imperfections including solid gel particles trapped within the film. All of the films had negative film ratings meaning that imperfections, gels and regions of poorly mixed polymer were readily observable to the naked eye. Commercially acceptable films have film ratings of +20 or higher, preferably at least +30.

Test Methods

Density

Resin density was measured by the Archimedes displacement method, ASTM D 792-00, Method B, in isopropanol. Specimens were measured within one hour of molding, after conditioning in the isopropanol bath at 23°C, for 8 minutes, to achieve thermal equilibrium prior to measurement. The specimens were compression molded according to ASTM D-4703-00, Annex A, with a five minutes initial heating period at about 190ºC, and a 15 ºC/min cooling rate per Procedure C. The specimen was cooled to 45ºC in the press, with continued cooling until "cool to the touch."

Melt Flow Rate by Extrusion Plastomer

Melt flow rate measurements for the ethylene-based polymers were performed according to ASTM D-1238-04, Condition 190°C/2.16 kg, Condition 190°C/5 kg and Condition 190°C/21.6 kg, which are known as I_2, I_5 and I_{21}, respectively. Melt flow rate is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt flow rate, although the relationship is not linear. Melt Flow Ratio (MFR) is the ratio of melt flow rate (I_{21}) to melt flow rate (I_2), unless otherwise specified.

Residual Metals

Titanium, aluminum and hafnium residuals were measured as ppm by wt using X-ray Diffraction techniques with appropriate standards.

Particle Size and Bulk Density

Particle size was measured using a standard set of mesh sieves — 10/18/35/60/120/200/pan with openings of 2000, 1000, 500, 250, 125 and 70 microns respectively and calculated using the mass of resin retained on each sieve. Fines are defined as resin particles on the 200 mesh screen and on the pan.

The Bulk Density measurement was a poured bulk density using a standard 500 cc volumetric cylinder.

The present invention may be embodied in other forms without departing from the spirit and the essential attributes thereof, and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

I claim:

1. A virgin granular polymer comprising polymer particles wherein at least 90% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1, and further wherein the virgin granular polymer has an I_{21} less than or equal to 70.

2. A virgin granular polymer comprising polymer particles wherein at least 90% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001, and further wherein the virgin granular polymer has an I_{21} less than or equal to 70.

3. The reaction product of polymerizing at least one olefin monomer in the presence of: (A) at least one catalyst precursor produced by contacting a Group 4 metal compound with one or more Titanium compounds selected from the group of $TiCl_3$ (Al-activated or hydrogen-reduced), and $Ti(OR)_4$ where R is ethyl, isopropyl or n-butyl in the presence of an alcohol solution comprising at least one C_2-C_4 alcohol and at least one of $MgCl_2$ and magnesium compounds which form $MgCl_2$ in the presence of the alcohol solution to form a catalyst precursor solution, forming said catalyst precursor solution into solid particles and subsequently halogenating the solid particles; and (B) at least one co-catalyst; wherein the reaction product comprises a granular polymer comprised of polymer particles and further wherein at least 90% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

4. The reaction product of Claim 3, wherein at least 95% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular

polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

5. The reaction product of Claim 3, wherein at least 93% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

6. The reaction product of polymerizing at least one monomer, in the gas phase, in the presence of: (A) at least one catalyst precursor produced by contacting a Group 4 metal compound with one or more Titanium compounds selected from the group of $TiCl_3$ (Al-activated or hydrogen-reduced), and $Ti(OR)_4$ where R is ethyl, isopropyl or n-butyl in the presence of an alcohol solution comprising at least one C_2-C_4 alcohol and at least one of $MgCl_2$ and magnesium compounds which form $MgCl_2$ in the presence of the alcohol solution to form a catalyst precursor solution, forming said catalyst precursor solution into solid particles and subsequently halogenating the solid particles; and (B) at least one co-catalyst; wherein the reaction product comprises a granular polymer comprised of polymer particles and further wherein at least 90% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001.

7. The reaction product of Claim 6, wherein at least 95% by weight of the granular polymer particles, have a density that is within two standard deviations of a mean density of the granular polymer, the ratio of the standard deviation of the mean density of the granular polymer to the mean density of the granular polymer is less than 0.002 and the ratio of the standard error of a linear fit to the mean of the density is less than 0.001.

8. The reaction product of Claim 3, wherein at least 93% by weight of the granular polymer particles, have an I_{21} that is within two standard deviations of a mean I_{21} of the granular polymer, the ratio of the standard deviation of I_{21} to the mean of the granular polymer is less than 0.2 and the ratio of the standard error of a linear fit to the mean of the granular polymer is less than 0.1.

9. Any one of the preceding Claims, wherein the granular polymer is produced in a two stage linked reactor system.

10. Any one of the preceding Claims, wherein the granular polymer is produced in a one stage reactor system.

11. Any one of the preceding Claims, wherein the granular polymer is produced in a fluidized bed reactor system.

12. Any one of the preceding Claims, wherein the granular polymer is produced in a slurry reactor system.

13. The virgin granular polymer of any one of Claims 1 and 2, wherein the virgin granular polymer has an I_{21} less than or equal to 30.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/067937

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F10/00
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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 20 April 2012	Date of mailing of the international search report 04/05/2012
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/067937

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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