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SPRUSON&FERGUSON

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Patent Request : Standard Patent

We, the Applicant/Nominated Person specified below, request we be granted a patent for the invention disclosed in the accompanying standard complete specification.

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[54] **Invention Title:**
Silica Supported Transition Metal Catalyst

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Details of Basic Application

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[33] **Country:** United States of America
[32] **Application Date:** 20 March 1992

Divisional Application Details

[62] **Original Application No:** 12574/92
Person by whom made: The Dow Chemical Company

DATED this Tenth Day of February 1997

The Dow Chemical Company

By:



Registered Patent Attorney

Australia

Patents Act 1990

Notice Of Entitlement

I, Colin Lewis Bodkin, of 31 Market Street, Sydney, New South Wales, 2000, Australia, Patent Attorney for the Applicant/Nominated Person in respect of Application No. 39332/93, state the following:-

The Applicant/Nominated Person has entitlement from the actual inventors as follows:

The Applicant/Nominated Person is the assignee of the actual inventors.

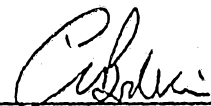
The Applicant/Nominated Person is entitled to rely on the basic application listed in the Patent Request as follows:

The Applicant/Nominated Person is the assignee of the basic applicant.

The basic application listed on the Patent Request is not the first application made in a Convention country in respect of the invention. Certain aspects of the invention were first disclosed in Application No. 07/644,053 filed in the United States of America on 18 January 1991 or in Australian Patent Application No. 12574/92. Convention priority is only claimed in respect of aspects of the present application which were first disclosed in the basic application listed on the Patent Request.

The Applicant/Nominated Person is the applicant/patentee of the original application/patent.

DATED this Tenth Day of February 1997



Colin Lewis Bodkin



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- (54) Title
SILICA SUPPORTED TRANSITION METAL CATALYST
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- (57)

Yet another aspect of the present invention is to provide ethylene/ α -olefin copolymers which are particularly effective in making films, especially cast films used in pallet wrapping applications. The copolymers are advantageously made using the catalyst compositions and process described herein. The copolymers can be used, e.g., as a core layer in a multilayer coextruded cast film structure, or they can be used by themselves in the film. The specific copolymers have a high density fraction greater than 17 percent and a molecular weight distribution (indicated by Mw/Mn) of less than 3.6 and, when converted into film form, provide greater overall film stretchability and puncture resistance.

CLAIM

1. A process for varying the short chain branching distribution (SCBD) of ethylene/ α -olefin copolymers characterized by (I) subjecting ethylene and one or more α -olefin comonomers to solution polymerization conditions in the presence of a catalyst composition comprising (A) a supported transition metal containing catalyst component comprising the product resulting from contacting (1) a porous solid inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than about 5 millimoles of hydroxyl groups per gram of support material and a particle size less than 10 microns and a surface area of from about 50 to about 800m²/g; (2) an organomagnesium compound

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hydrocarbon soluble organomagnesium alkoxide or hydrocarbon soluble magnesium dialkoxide; (3) a titanium compound; optionally (4) a vanadium compound; and (5) a Group IIIA metal alkyl halide; and wherein the components are employed in amounts which provide the following atomic ratios:

- Si + Al:Mg of from about 1:1 to about 40:1;
 - Mg:Ti of from about 0.2:1 to about 20:1;
 - Mg:V of from about 0.2:1 to about 20:1 when V is present;
 - Mg:IIIA metal of from about 0.05:1 to about 10:1;
 - V:Ti of from about 0.8:1 to about 1.2:1 when V is present; and
- (B) a cocatalyst or activator for component (A); and
- (II) controlling the SCBD by varying the ratio of Mg:Ti in component (A).



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(54) Title: SILICA SUPPORTED TRANSITION METAL CATALYST

(57) Abstract

A transition metal containing catalyst useful for the polymerization of α -olefins is prepared by (A) forming in an inert atmosphere which excludes oxygen and moisture a slurry of (1) a porous inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than about 5 millimoles of hydroxyl groups per gram of support material and a particle size not greater than about 10 microns and a surface area of from about 50 to about 800 m²/g in an inert organic liquid medium; (B) mixing said slurry with (2) an alkoxide and stirring the resultant mixture at a temperature of from about -20 °C to about 120 °C for a time sufficient to saturate the surface of the support material; (C) mixing the product from (B) with (3) a titanium compound or a combination of a titanium compound and (4) a vanadium compound and stirring the resultant mixture at a temperature of from about -20 °C to about 120 °C for a time sufficient to allow complete reaction of the titanium compound and the vanadium compound with the organomagnesium moieties remaining on the solid support; (D) mixing the product from (C) with an inert organic solution of (5) a Group IIIA metal alkyl halide at a temperature of from about -20 °C to about 120 °C for a time sufficient to complete the reduction of the titanium and vanadium, if present, compounds to their final oxidation state. Ethylene/ α -olefin copolymers which have greater than 17 percent high density fraction and an M_w/M_n ratio of less than about 3.6 are shown to be useful in making cast films which have good stretchability and good puncture resistance. Copolymers of the present invention having the specified properties are especially useful in making the films.



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(54) Title: SILICA SUPPORTED TRANSITION METAL CATALYST

(57) Abstract

A transition metal containing catalyst useful for the polymerization of α -olefins is prepared by (A) forming in an inert atmosphere which excludes oxygen and moisture a slurry of (1) a porous inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than about 5 millimoles of hydroxyl groups per gram of support material and a particle size not greater than about 10 microns and a surface area of from about 50 to about 800 m²/g in an inert organic liquid medium; (B) mixing said slurry with (2) an alkoxide and stirring the resultant mixture at a temperature of from about -20 °C to about 120 °C for a time sufficient to saturate the surface of the support material; (C) mixing the product from (B) with (3) a titanium compound or a combination of a titanium compound and (4) a vanadium compound and stirring the resultant mixture at a temperature of from about -20 °C to about 120 °C for a time sufficient to allow complete reaction of the titanium compound and the vanadium compound with the organomagnesium moieties remaining on the solid support; (D) mixing the product from (C) with an inert organic solution of (5) a Group IIIA metal alkyl halide at a temperature of from about -20 °C to about 120 °C for a time sufficient to complete the reduction of the titanium and vanadium, if present, compounds to their final oxidation state. Ethylene/alpha-olefin copolymers which have greater than 17 percent high density fraction and an M_w/M_n ratio of less than about 3.6 are shown to be useful in making cast films which have good stretchability and good puncture resistance. Copolymers of the present invention having the specified properties are especially useful in making the films.

SILICA SUPPORTED TRANSITION METAL CATALYST

The present invention pertains to solid inorganic oxide (e.g., silica) supported transition metal catalysts, a process for polymerizing olefins in their presence, polymers made
5 by this polymerization process and films made from some specific polymers.

The polymerization of ethylene and the copolymerization of ethylene with other olefins is known to be carried out by gas phase, solution and/or suspension (slurry) polymerization processes. Advantages of the solution process include short reaction times,
10 improved heat removal and monomer conversion for mass and energy control of polymerizations and single-phase reaction environments for controlling reaction dynamics. A most advantageous solution polymerization would be conducted at even higher reaction temperatures yet with a polymerization catalyst that yields sufficiently high molecular weight polymers with a high catalyst efficiency at these higher temperatures which lowers catalyst
15 residues in the product and/or permits complete omission of the catalyst removal step.

In the suspension (slurry) polymerization of olefins, the advantages are low pressures, low temperatures and the ability to make very high molecular weight polymers. It is advantageous to carry out these reactions with sufficiently high polymerization efficiencies
20 such that residues from the polymerization catalyst do not have to be removed from the resulting polymer.

There are many polymerization catalysts for suspension polymerization known in the art. Hagerty et al. in U.S. Patent 4,562,169 disclose the preparation of a supported catalyst
25 by treating a solid porous carrier having reactive OH groups such as silica in a liquid medium with an organomagnesium compound to react with the OH groups on the carrier; evaporating said liquid to precipitate magnesium onto the carrier and recovering a supported magnesium composition in the form of a dry, free-flowing powder; reacting the powder with a tetravalent titanium compound in a liquid medium. The catalyst is useful in the polymerization of olefins.

30 Nowlin in U.S. Patent 4,593,009 and U.S. Patent 4,672,096 discloses a catalyst for polymerizing olefins which catalyst is prepared by treating a carrier containing OH groups with an organomagnesium composition and contacting the thus-formed magnesium-containing carrier with a solution of at least one tetravalent vanadium compound or a solution containing
35 both a vanadium compound and a titanium compound

Gessel in U.S. 4,244,838 describes catalysts prepared from an organomagnesium compound, an organic hydroxyl-containing material and a transition metal halide. These solids produced by this reaction are isolated and washed prior to use in a polymerization.

5 Fuentes et al. in U.S. 4,544,647 disclose catalyst compositions prepared from an organomagnesium material, an organic hydroxyl-containing material, a reducing halide source and a transition metal compound

Marchand et al. in U.S. 4,910,272 describe a process for polymerizing olefins in the
10 presence of a catalyst prepared from an inorganic oxide, an organomagnesium material, an organic hydroxyl-containing material, a reducing halide source and a transition metal compound.

The catalyst efficiency of these catalysts is, in general, decreased with increased
15 polymerization temperatures, specifically temperatures above 140°C.

The catalysts known for solution polymerization comprise an organomagnesium component, an aluminum halide and/or an additional halide source and a transition metal compound. Lowery et al in US 4,250,288 describes such compositions that are useful in the
20 polymerization of α -olefins above 140°C.

Sakurai et al. in U.S. 4,330,646 describes similar catalysts containing a titanium or a titanium and/or a vanadium compound as the transition metal component. These catalysts are useful at polymerization temperatures of at least 180°C. The disadvantage of these
25 catalysts is that the reactions that produce the catalyst solids are highly exothermic and difficult to control and reproduce. These catalyst compositions also contain a large excess of halide with respect to the transition metal component and yield polymers with a relatively high halide content. The composition as a whole is used directly in the polymerization of olefins.

30 It is well known in the art to optimize the properties of linear low density polyethylene (LLDPE) by variation in product molecular weight, molecular weight distribution (MWD) and density to match the required product application. Increasing the molecular weight, narrowing the MWD or lowering the density of LLDPE usually results in improved impact strength and puncture resistance properties. Molecular weight of the polymer prepared
35 in Ziegler Natta catalyzed processes (as described by Professor Karl Ziegler in U.S. Pat. Nos. 3,113,115 and 3,257,332) is typically controlled in the process by the addition of varying amounts of telogens most commonly hydrogen. Similarly the density of the product is typically controlled by varying the comonomer concentration in the reaction medium.

In addition to optimizing product molecular weight and density for a given product application further improvement in resin performance can be obtained by narrowing the molecular weight distribution of a given melt index and density product. U.S. patent No. 5 4,612,300 describes a process for preparing LLDPE copolymers with narrow molecular weight distribution using a specific catalyst formulation, resulting in polymers for film applications with improved clarity and toughness

Yet another property known to improve the clarity and toughness of alpha-olefin 10 polymers is a small spherulite size as described for polypropylene (Kuhre et al, SPE Journal, Oct, 1964, pps 1113 - 1119) and polyethylene (Narh et al, J. Mat. Sci, 15 (1980), pps 2001 - 2009). Similarly, U.S. Patent No. 4,205,021 discloses copolymers with densities from 0.90 to 0.94 g/cm³ with exceedingly high weight average molecular weight but with the intrinsic viscosities of conventional ethylene copolymers and spherulite sizes of not more than six microns.

15

Linear low density polyethylene (LLDPE) produced with Ziegler catalysts have side groups introduced into the molecule from copolymerization with comonomers. In the case of 1-octene this side group would have six carbons atoms i.e. a hexyl chain. The distribution of these side groups or branches along and among all the polymer molecules is known as the 20 polymer Short Chain Branching Distribution (SCBD) and the nature of this distribution has a strong impact on product properties and performance

J. Plastic Film and Sheeting, Vol 4, July 1988, pps 214 - 226, "Short Chain Branching Distribution of ULDPE", K Dohrer L.G. Hazlitt, N.F. Whiteman), teaches that LLDPE copolymers 25 prepared using a catalyst known to produce narrow molecular weight distribution LLDPE copolymers with a density greater than 0.87 but less than 0.918 g/cm³ have unexpectedly improved (lower) amounts of n-hexane extractables than those from similar density products of other catalysts when having a narrow SCBD. Also in this study, a quantitative measurement of SCBD was introduced, the z_1/z_0 or simply the z ratio. By this definition, polymers of similar 30 densities should have similar values of z_1 but polymers with a broader SCBD will have a lower value of z_0 . Therefore if z_1/z_0 is low the SCBD is narrow and vice versa.

U.S. Patent No 4,438,238 discloses ethylene/alpha olefin copolymers with improved properties formed by mixing copolymers of high molecular weight and specified SCB 35 (short chain branches/1000 carbons) with copolymers of lower molecular weight and specified SCB results in resins of 0.91 to 0.94 g/cm³ density and melt index of 0.02 to 50 g/10 min and melt flow ratio of 35 to 250 with excellent strength properties

U.S. Patent No. 4,918,038 discloses a process for the production of ethylene homopolymers or copolymers with a broad and/or bimodal molecular weight distribution using a mixed catalyst system. One advantage of this system is that the product can be made in a single reactor rather than using multistage reactors which raise questions of efficiency and cost.

5

U.S. Patent No. 4,481,342 teaches a method of preparing an ethylene/alpha olefin copolymer of varying alpha olefin content, the incorporation of which is controlled by the porosity and pore radius of the magnesium chloride support.

10

U.S. Patent No. 4,522,987 discloses a process using a chromium based catalyst system in which the incorporation of comonomer into the polymer chain occurs in a "super-random" fashion as described by the relative comonomer dispersity (RMD) as determined by N.M.R. The dispersity is controlled by the nature of the comonomer and varying its concentration in mole percent in the gas phase.

15

U.S. Patent No. 3,645,992 discloses a continuous process for the preparation of homogeneous random partly crystalline copolymers of narrow MWD. The degree of homogeneity is controlled by varying the reactor temperature. Similarly homogeneity was decreased when R_2AlCl was used as cocatalyst rather than $R_{1.5}AlCl_{1.5}$ or $RAlCl_2$. Similarly increasing the ratio of cocatalyst to catalyst to greater than 9:1 for octene copolymers was required to yield homogeneous copolymers

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It would be desirable to have available catalyst compositions which exhibit significantly higher polymerization efficiencies based on the transition metal and the halide. It would also be desirable to have available catalyst compositions which exhibit these high efficiencies while being prepared in a manner which did not require the isolation and/or washing of the solid catalytic product. It would be further desirable to ease the process of preparation of the catalyst in order to increase reproducibility and quality of the catalyst

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It would also be desirable to have available such catalysts which would provide polymers having a high molecular weight and a relatively narrow molecular weight distribution and which exhibit more tolerance to hydrogen at polymerization temperatures of at least 180°C and even greater than 200°C

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Also, it would be advantageous to have a solution process which, at a given melt index and density, results in a narrow molecular weight distribution product with small spherulite size, the SCBD (short chain branching distribution) of which, can be easily controlled to yield the desired combination of polymer properties for the specific product application.

One aspect of the present invention pertains to a supported transition metal catalyst component which comprises an inert liquid medium having slurried therein a composition comprising the product resulting from contacting (1) a porous solid inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than 5 millimoles of hydroxyl groups per gram of support material and a particle size not greater than 10 microns and a surface area of from 50 to 800 m²/g; (2) a hydrocarbon soluble organomagnesium alkoxide or hydrocarbon soluble magnesium dialkoxide; (3) a titanium compound; optionally (4) a vanadium compound; and (5) a Group IIIA metal alkyl halide; and wherein the components are employed in amounts which provide the following atomic ratios:

Si + Al (from the inorganic oxide support):Mg of from 1:1 to 30:1;
Mg:Ti of from 0.2:1 to 10:1;
Mg:V of from 0:1 to 10:1;
Mg:IIIA metal of from 0.05:1 to 5:1; and
V:Ti of from 0:1 to 5:1.

Another aspect of the present invention pertains to a process for preparing a supported transition metal catalyst component slurried in an inert liquid medium, which process comprises (A) forming in an inert atmosphere which excludes oxygen and moisture a slurry of (1) a porous inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than 5 millimoles of hydroxyl groups per gram of support material and a particle size not greater than 10 microns and a surface area of from 50 to 800 m²/g in an inert organic liquid medium; (B) mixing said slurry with (2) a hydrocarbon soluble organomagnesium alkoxide or hydrocarbon soluble magnesium dialkoxide and stirring the resulting mixture at a temperature of from -20°C to 120°C for a time sufficient to saturate the surface of the support material; (C) mixing the product from (B) with (3) a titanium compound or a combination of a titanium compound and (4) a vanadium compound or adding the titanium compound and vanadium compound separately and stirring the resultant mixture at a temperature of from -20°C to 120°C for a time sufficient to allow complete reaction of the titanium compound and the vanadium compound with the organomagnesium moieties remaining on the solid support; (D) mixing the product from (C) with an inert organic solution of (5) a Group IIIA metal alkyl halide at a temperature of from -20°C to 120°C for a time sufficient to complete the reduction of the titanium and vanadium, if present, compounds to their final oxidation state

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A further aspect of the present invention pertains to a process for polymerizing one or more α -olefins and optionally one or more polymerizable ethylenically unsaturated compounds other than an α -olefin which process comprises contacting the materials to be

polymerized with (A) a supported transition metal containing catalyst component comprising the product resulting from contacting (1) a porous inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than 5 millimoles of hydroxyl groups per gram of support material and a particle size less than 10 microns and a surface area of from 50 to 800 m²/g; (2) a hydrocarbon soluble organomagnesium alkoxide or hydrocarbon soluble magnesium dialkoxide; (3) a titanium compound; optionally (4) a vanadium compound; and (5) a Group IIIA metal alkyl halide; and wherein the components are employed in amounts which provide the following atomic ratios:

10 Si + Al:Mg of from 1:1 to 30:1;
 Mg:Ti of from 0.2:1 to 10:1;
 Mg:V of from 0.2:1 to 10:1;
 Mg:IIIA metal of from 0.05:1 to 5:1;
 V:Ti of from 0:1 to 5:1; and

15 (B) a cocatalyst or activator for component (A).

Still another object of the present invention pertains to process for varying the short chain branching distribution (SCBD) of ethylene/ α -olefin copolymers which comprises (I) subjecting ethylene and one or more α -olefin comonomers to solution polymerization conditions in the presence of a catalyst composition comprising (A) a supported transition metal containing catalyst component comprising the product resulting from contacting (1) a porous inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than 5 millimoles of hydroxyl groups per gram of support material and a particle size less than 10 microns and a surface area of from 50 to 800 m²/g; (2) a hydrocarbon soluble organomagnesium alkoxide or hydrocarbon soluble magnesium dialkoxide; (3) a titanium compound; optionally (4) a vanadium compound; and (5) a Group IIIA metal alkyl halide; and wherein the components are employed in amounts which provide the following atomic ratios:

30 Si + Al:Mg of from 1:1 to 30:1;
 Mg:Ti of from 0.2:1 to 10:1;
 Mg:V of from 0.2:1 to 10:1;
 Mg:IIIA metal of from 0.05:1 to 5:1;
 V:Ti of from 0.8:1 to 1.2:1; and

(B) a cocatalyst or activator for component (A); and
 35 (II) controlling the SCBD by varying the ratio of Mg:Ti in component (A)

The present invention provides catalyst compositions which exhibit high polymerization efficiencies based on the transition metal and the halide and are prepared in a

manner which do not require the isolation and/or washing of the solid catalytic product. The catalysts which contain vanadium produce a polymer having a high molecular weight and a relatively narrow molecular weight distribution when the polymers are prepared by the solution process

5

The present invention provides catalyst compositions which exhibit high polymerization efficiencies based on the transition metal and the halide and are prepared in a manner which do not require the isolation and/or washing of the solid catalytic product. The catalysts which contain vanadium produce a polymer having a relatively broad molecular weight distribution when the polymers are prepared by the slurry process.

10

The present invention also provides a process for preparing ethylene/ α -olefin copolymers which at a given melt index and density results in a narrow molecular weight distribution product with small spherulite size and controlling the short chain branching distribution by varying the Mg:Ti atomic ratio so as to produce copolymers with a desired combination of polymer properties for specific product applications.

15

Yet another aspect of the present invention is to provide ethylene/ α -olefin copolymers which are particularly effective in making films, especially cast films used in pallet wrapping applications. The copolymers are advantageously made using the catalyst compositions and process described herein. The copolymers can be used, e.g., as a core layer in a multilayer coextruded cast film structure, or they can be used by themselves in the film. The specific copolymers have a high density fraction greater than 17 percent and a molecular weight distribution (indicated by M_w/M_n) of less than 3.6 and, when converted into film form, provide greater overall film stretchability and puncture resistance.

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All references herein to elements or metals belonging to a certain Group refers to the Periodic Table Of The Elements published by the Sargent-Welch Scientific Company, Skokie Illinois, catalog number S-18806 (1968)

30

The term "hydrocarbyl" as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic, aryl substituted cycloaliphatic, aliphatic substituted aromatic or aliphatic substituted cycloaliphatic groups

35

The term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached

The term "copolymer" as employed herein means a polymer produced by polymerizing a mixture of two or more polymerizable ethylenically unsaturated monomers.

PREPARATION OF TRANSITION METAL CATALYST

5

The transition metal catalyst of the present invention can be prepared in the following manner.

The porous inorganic oxide support material is slurried in an inert organic diluent
10 under conditions which exclude oxygen (air) and moisture at a temperature of from -20°C to 120°C, preferably from 0°C to 100°C, more preferably from 20°C to 70°C. No particular time is required other than that to form a uniform slurry of the support in the diluent. This depends upon the amounts involved, but usually a good uniform slurry can be formed in 1 hour in a concentration range from 0.1 to 15, preferably from 0.5 to 10, more preferably from 1 to 7,
15 weight percent.

To this slurry is then added the hydrocarbon soluble organo magnesium alkoxide or hydrocarbon soluble magnesium dialkoxide, again under conditions which exclude oxygen (air) and moisture, and the mixture stirred at a temperature of from -20°C to 120°C, preferably
20 from 0°C to 100°C, more preferably from 20°C to 70°C for a time sufficient to react the magnesium compound with surface of the solid support, usually from 0.1 to 10, preferably from 0.2 to 8, more preferably from 0.5 to 4, hours

After the above addition of the magnesium compound, a titanium compound or
25 a combination of a titanium compound and a vanadium compound is added, again under conditions which excludes oxygen (air) and moisture, and the mixture stirred at a temperature of from -20°C to 120°C, preferably from 0°C to 100°C, more preferably from 20°C to 70°C for a time sufficient to completely react the titanium compound and the vanadium compound with the reactive silica and magnesium functionalities, usually from 0.1 to 100, preferably from 0.5
30 to 20, more preferably from 1 to 10, hours. The titanium and vanadium compounds can be premixed prior to their addition or they can be added separately in any order to the product resulting from blending the magnesium compound with the slurry of the inorganic oxide support material

35 Following the addition and mixing of the titanium and/or vanadium compounds, a Group IIIA metal alkyl halide is added and the mixture is stirred at a temperature of from -20°C to 120°C, preferably from 0°C to 100°C, more preferably from 20°C to 70°C for a time sufficient to reduce the titanium compound and vanadium compound, if present, to their final

oxidation states, usually from 1 to 100, preferably from 2 to 50, more preferably from 5 to 20, hours.

5 Upon completion of the addition and mixing of the Group IIIA metal alkyl halide, the thus formed transition metal catalyst component can be employed in the polymerization of α -olefins as is without isolation of the solid components from the liquid components. The transition metal catalyst component can be employed immediately upon its preparation or the component can be stored under inert conditions for some length of time, usually for periods of time as long as 90 days.

10

The components can also, if desired, be added in the order as follows: SiO_2 + Mg compound + Ti compound + Al compound + V compound.

15 The components can also, if desired, be added in the order as follows: SiO_2 + Mg compound + Al compound + Ti compound + V compound.

Oxygen (air) and moisture can be excluded during catalyst preparation by conducting the preparation in an inert atmosphere such as, for example, nitrogen, argon, xenon or methane.

20

COMPONENTS OF THE TRANSITION METAL CATALYST

Porous Support Material

25 Suitable porous silica or alumina support materials which can be employed herein include, those containing not greater than 5, preferably not greater than 4, more preferably not greater than 3, millimoles of hydroxyl groups (OH) per gram of support material. These hydroxyl (OH) groups are isolated silanol groups on the silica surface

30 The hydroxyl groups can be reduced or eliminated by treating the support material either thermally or chemically. Thermally, the support material can be heated at temperatures of from 250°C to 870°C , more preferably from 600°C to 800°C for a time sufficient to reach the equilibrium hydroxyl group concentration, usually from 1 to 24, preferably from 2 to 20, more preferably from 3 to 12, hours

35 The hydroxyl (OH) groups can be removed or reduced chemically by treating the support material with SiCl_4 , chlorosilanes, silylamines, or any combination thereof at a temperature of from -20°C to 120°C , more preferably from 0°C to 40°C for a time sufficient to reduce the hydroxyl content to the desired value, usually less than 30 minutes

The porous support material has a particle size of not greater than 10, preferably from 0.1 to 10, more preferably from 1 to 9, most preferably from 2 to 8, microns and a surface area in the range of from 50 to 800, preferably from 150 to 600, more preferably from 300 to 500, m^2/g .

5

The particle size of the support is important as it has been discovered that lowering the particle size of the support below 10 microns while maintaining the support surface area and porosity results in an unexpected increase in the catalyst productivity and hence a reduction in product chloride and titanium residues relative to products of the same
10 catalyst made on a support of equivalent surface area and porosity but larger particle size.

Inert Liquid Diluent

Suitable inert liquid diluents which can be employed to slurry the inorganic oxide
15 support material and as a diluent for any of the other components employed in the preparation of the catalyst include, for example, aliphatic hydrocarbons, aromatic hydrocarbons, naphthinic hydrocarbons, or any combination thereof. Particularly suitable solvents include, for example, pentane, isopentane, hexane, heptane, octane, isooctane, nonane, isononane, decane, cyclohexane, methylcyclohexane, toluene, or any combination of
20 any two or more of such diluents.

Magnesium Compound

Suitable magnesium compounds which can be employed in the preparation of
25 the transition metal catalyst component include, for example, those hydrocarbon soluble organomagnesium compounds represented by the formulas $R_xMg(OR)_y$; wherein each R is independently a hydrocarbyl group having from 1 to 20, preferably from 1 to 10, more preferably from 2 to 8, carbon atoms; $x + y = 2$; and $0.5 \leq y \leq 2$. Preferably, x has a value of zero or 1 and y has a value of 1 or 2 and most preferably, x has a value of 1 and y has a value of 1.

30

Particularly suitable magnesium compounds include, for example, n-butylmagnesium butoxide, ethylmagnesium butoxide, butylmagnesium ethoxide, octylmagnesium ethoxide, butylmagnesium i-propoxide, ethylmagnesium i-propoxide, butylmagnesium n-propoxide, ethylmagnesium n-propoxide, s-butylmagnesium butoxide,
35 butylmagnesium 2,4-dimethylpent-3-oxide, n-butylmagnesium octoxide, s-butylmagnesium octoxide, or any combination thereof

Also suitable are the hydrocarbon soluble reaction product (dialkoxide) of a magnesium dihydrocarbyl (MgR_2) compound and an oxygen-containing compound (ROH) such as, for example, an aliphatic or cycloaliphatic or acyclic C_5 - C_{18} beta or gamma alkyl-substituted secondary or tertiary monohydric alcohol, as disclosed by Kamienski in U.S. Patent 4,748,283 which is incorporated by reference. The reaction is preferably conducted in the presence of a liquid hydrocarbon media. The alcohol is usually employed in slightly more than twice the molar equivalent, based on magnesium. The reaction is usually conducted at temperatures not in excess of $50^\circ C$, preferably below $40^\circ C$. Particularly suitable oxygen containing compounds include, for example, 2,4-dimethyl-3-pentanol, 2,3-dimethyl-2-butanol, 2,4-dimethyl-3-hexanol, 2,6-dimethyl-4-heptanol, 2,6-dimethyl-cyclohexanol, or any combination thereof. Particularly suitable magnesium dialkyl compounds include, for example, butylethylmagnesium, dibutylmagnesium, dihexylmagnesium, butyloctylmagnesium, any combination thereof.

15 Titanium Compound

Suitable titanium compounds which can be employed in the preparation of the transition metal catalyst component include, for example, those represented by the formula $TiX_{4-a}(OR')_a$; wherein each R' is independently an alkyl group having from 1 to 20, preferably from 1 to 10, more preferably from 2 to 8, carbon atoms and a halogen atom, preferably chlorine; and a has a value from zero to 4. Particularly suitable titanium compounds include, for example, titanium tetrachloride ($TiCl_4$), titanium tetraisopropoxide ($Ti(O-i-C_3H_7)_4$), titanium tetraethoxide ($Ti(OC_2H_5)_4$), titanium tetrabutoxide ($Ti(OC_4H_9)_4$), titanium triisopropoxidechloride ($Ti(O-i-C_3H_7)_3Cl$), or any combination thereof.

25

Vanadium Compound

In the solution process, when it is desirable to produce α -olefin polymers which have a high molecular weight and a relatively narrower molecular weight distribution than that produced with the catalyst containing only titanium as the transition metal, a vanadium compound can be added as a portion of the transition metal component during preparation of the catalyst. A narrowing of the molecular weight distribution is indicated by a lowering of the I_{10}/I_2 value of the polymer.

35

By the term "relatively narrow molecular weight distribution" it is meant that the resulting polymer produced in the presence of a catalyst containing both titanium and vanadium has a narrower molecular weight distribution than the polymer produced under similar conditions with a similar catalyst prepared without the vanadium component.

In the slurry process when it is desirable to produce α -olefin polymers which have a high molecular weight and a relatively broad molecular weight distribution than that produced with the catalyst containing only titanium as the transition metal, a vanadium compound can be added as a portion of the transition metal component during preparation of the catalyst. A broadening of the molecular weight distribution is indicated by an increase of the I_{20}/I_2 , high load melt flow ratio (HLMFR), value of the polymer.

By the term "relatively broad molecular weight distribution" it is meant that the resulting polymer produced in the presence of a catalyst containing both titanium and vanadium has a broader molecular weight distribution than the polymer produced under similar conditions with a similar catalyst prepared without the vanadium component.

Suitable vanadium compounds which can be employed in the preparation of the transition metal catalyst include, for example, those represented by the formulas VX_4 and $V(O)X_3$; wherein each X is independently OR or a halogen atom, preferably chlorine; each R is independently an alkyl group having from 1 to 20, preferably from 2 to 8, more preferably from 2 to 4, carbon atoms. Particularly suitable vanadium compounds include, for example, vanadium tetrachloride (VCl_4), vanadium trichloride oxide ($V(O)Cl_3$), vanadium triisopropoxide oxide ($V(O)(O-i-C_3H_7)_3$), vanadium triethoxide oxide ($V(O)(OC_2H_5)_3$), or any combination thereof.

Organo Halide Compounds of a Group IIIA Metal

Suitable organo halide compounds of a group IIIA Metal which can be employed in the preparation of the transition metal catalyst include, for example, those represented by the formula R'_yMX_z ; wherein M is a metal from Group IIIA of the Periodic Table of the Elements, preferably aluminum or boron; each R' is independently an alkyl group having from 1 to 20, preferably from 1 to 10, more preferably from 2 to 8, carbon atoms; X is a halogen atom, preferably chlorine; y and z each independently have a value from 1 to a value equal to the valence of M minus 1 and y + z has a value equal to the valence of M. Particularly suitable such organo halide compounds include, for example, ethylaluminum dichloride, ethylaluminum sesquichloride, diethylaluminum chloride, isobutylaluminum dichloride, diisobutylaluminum chloride, octylaluminum dichloride, or any combination thereof.

Component Amounts

For use in the solution process, the components are employed in quantities which provide an atomic ratio as follows:

Si and/or Al(from the inorganic oxide support):Mg of from 1:1 to 50:1, preferably from 2:1 to 40:1, more preferably from 4:1 to 20:1;

5 Mg:group IIIA metal of from 0.01:1 to 100:1, preferably from 0.05:1 to 10:1, more preferably from 0.1:1 to 5:1.

Mg:Ti of from 0.05:1 to 40:1, preferably from 0.1:1 to 20:1, more preferably from 0.2:1 to 10:1;

10 Mg:V, when V is present, of from 0.05:1 to 40:1, preferably from 0.1:1 to 20:1, more preferably from 0.2:1 to 10:1;

V:Ti of from 0:1 to 20:1, preferably from 0.1:1 to 10:1, more preferably from 0.2:1 to 5:1.

15

However, when it is desired to employ the solution process to vary the short chain branching distribution (SCBD) of ethylene/ α -olefin copolymers, the V:Ti atomic ratio is from 0.8:1 to 1.2:1, preferably 1:1. For making the copolymers useful for making films of the present invention which have good stretchability and puncture, the V:Ti ratio should also be

20

For use in the suspension (slurry) process, the components are employed in quantities which provide an atomic ratio as follows:

25 Si and/or Al(from the inorganic oxide support):Mg of from 1:1 to 50:1, preferably from 2:1 to 40:1, more preferably from 4:1 to 20:1;

Mg:group IIIA metal of from 0.01:1 to 100:1, preferably from 0.05:1 to 10:1, more preferably from 0.1:1 to 5:1.

30

Mg:Ti of from 0.05:1 to 40:1, preferably from 0.1:1 to 20:1, more preferably from 0.2:1 to 10:1;

35 Mg:V, when V is present, of from 0.05:1 to 40:1, preferably from 0.1:1 to 20:1, more preferably from 0.2:1 to 10:1;

V:Ti of from 0:1 to 20:1, preferably from 0.1 to 10:1, more preferably from 0:1 to 3:1.

The compound employed as the liquid medium can be employed in any amount which provides the catalyst component with the desired consistency which does not interfere with the polymerization behavior of the catalyst.

5

COCATALYST or ACTIVATOR

The transition metal catalyst component described above requires a cocatalyst or activator in order to efficiently polymerize the α -olefin monomer(s). Suitable cocatalysts or
10 activator compounds include, for example, Group IIIA metal alkyl, metal alkoxide or metal alkyl halide compounds, particularly C₁-C₁₀ alkyl compounds of aluminum. Particularly suitable such compounds include, for example, triethylaluminum, trimethylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, diethylaluminum chloride, diethylaluminum ethoxide, or any combination of any two or more of such compounds.

15

Also suitable are the aluminoxanes such as those represented by the formula $(Al(O)R)_x$; wherein R is an alkyl group having from 1 to 8 carbon atoms and x has a value greater than 4. Particularly suitable aluminoxanes include, for example, methylaluminoxane, hexaisobutyltetraluminoxane, or any combination of any two or more of such compounds.
20 Also, mixtures of these aluminoxanes with alkyl aluminum compounds such as, for example, triethylaluminum or tributylaluminum can be employed.

The cocatalyst or activator compound can be employed in the solution process in amounts which provide a ratio of atoms of Group IIIA metal per combined atoms of Ti and V of
25 from 0.1:1 to 50:1, preferably from 1:1 to 20:1, more preferably from 2:1 to 15:1.

The cocatalyst or activator compound can be employed in the suspension (slurry) process in amounts which provide a ratio of atoms of Group IIIA metal per combined atoms of Ti and V of from 1:1 to 1000:1, preferably from 5:1 to 500:1, more preferably from 10:1 to
30 200:1.

Altering the Properties of Ethylene/ α -olefin Copolymers by Controlling the Short Chain Branching Distribution in the Copolymer

35 The process of the present invention differs from those of the prior art in that it describes a solution process for controlling SCBD (as measured by the z-ratio) over a wide range of melt indices and densities and yielding in all resins a narrow molecular weight distribution and small spherulite size

According to the current invention a process for the control of the SCBD of these resins is achieved by systematic variation in the catalyst composition. This control is independent of support surface area and does not require changes in reactor temperature or deviations from optimum cocatalyst/ catalyst ratio ensuring optimum catalyst productivity. The process can be used for preparing as one example cast film resins with improved stretch performance or blown film resins with improved strength properties such as dart impact.

The process of the current invention systematically varies the magnesium:titanium ratio of the silica supported catalyst to yield products of a given melt index and density with narrow molecular weight distribution and small spherulite size. The surprising results of our investigation has demonstrated that in the continuous solution process, for the preparation of a given melt index and density, systematically increasing or decreasing the magnesium:titanium ratio of the catalyst while maintaining the catalyst titanium:vanadium molar ratio at 1:1 results in a systematic broadening (i.e., decrease the Mg:Ti ratio) or narrowing (i.e., increase the Mg:Ti ratio) of the product SCBD as measured by the z ratio (z_1/z_0) of these resins.

The application of this process to resins of various melt index and density allows the product SCBD, z-ratio and crystallization temperature to be tailored to the specific product application with resulting improvements in resin physical properties. In the course of this investigation we have also unexpectedly discovered that variations in the catalyst yields resins, which, when made into films, demonstrate improved stretchability and puncture resistance, particularly from narrow molecular weight distribution, broader SCBD LLDPE resins.

This process is conducted at solution conditions described elsewhere in this application.

The copolymers produced by this process are ethylene/alpha olefin copolymers of the polymerizable comonomers with melt index from 0.2 to 500 grams/10 minutes (ASTM D 1238, Condition 190°C/2.16 kg), preferably from 0.4 to 100 or more preferably from 0.6 to 5; and a density from 0.8 to 0.96 g/cm³ (ASTM D 792), preferably from 0.85 to 0.94 g/cm³, more preferably from 0.90 to 0.93 g/cm³

Fabricated articles such as molded articles (e.g., injection molded, blow molded, roto molded and compression molded parts) can be made from the copolymers produced by this invention. Of particular utility, however, are films or multilayer film structures from the copolymers of the present invention. The films or film structures can be made using any of the

conventional film manufacturing processes. These include blown film, cast film and extrusion coated film processes. Especially preferred are cast films. The copolymers of the present invention can be used alone in the film (i.e., as a monolayer) or they can be used as at least one layer of a multilayer film structure. The films are usually from 0.4 mils to 1.2 mils in thickness, preferably 0.8 mils. Additives can also be included in the copolymers of the present invention for use in the films. For example, additives are often included in copolymers used to make films for pallet wrapping, an especially attractive use area for the copolymers described herein. The skin layer of the pallet wrapping films might contain special additives, e.g., polyisobutylene (PIB), to enhance cling properties of the film to the goods on the pallet.

10

We have found that specific properties of ethylene/alpha-olefin copolymers which, when made into films for use in pallet wrapping, enhance the ultimate stretchability and puncture properties of the film. High ultimate stretchability is desired to avoid or minimize film breakage, while good puncture properties minimizes film damage. The combination of good stretchability and good puncture also leads to good end user economics since less film is used, thereby minimizing waste. The desired ultimate stretchability is at least 280 percent, while maintaining a puncture of at least 250 ft-lbs/cm³. Ultimate stretchability is tested by simulated pallet wrapping conditions and is described further in this disclosure. The ethylene/alpha-olefin copolymers used to make pallet wrapping films will have a weight average molecular weight (M_w) to number average molecular weight (M_n) ratio (M_w/M_n) of less than 3.6, preferably less than 3.3, and a high density fraction greater than 17 percent (by weight of the copolymer), preferably at least 20 percent. The copolymers made using the catalysts and process described in the present invention which have these properties are especially effective in this stretch film application and have not been available here-to-fore.

Unblended ethylene/alpha-olefin copolymers having the above specified properties are also within the scope of this invention. The term "unblended" indicates that the copolymers are made within a single reactor system and do not have other polymers blended to them to attain the properties of narrow molecular weight distribution and percent high density fraction, with the exception of additives for other reasons, e.g., PIB for cling enhancement. For this stretch film application, the copolymers preferably have a density from 0.905 g/cm³ to 0.935 g/cm³, especially from 0.912 g/cm³ to 0.925 g/cm³. The melt index of the copolymers is preferably from 0.6 grams/10 minutes to 6 grams/10 minutes, especially from 1 gram/10 minutes to 4 grams/10 minutes.

35

POLYMERIZABLE MONOMERS

Suitable polymerizable monomers include, for example α -olefins having from 2 to 20, preferably from 2 to 12, more preferably from 2 to 8, carbon atoms and any combination of any two or more of such α -olefins. Particularly suitable such α -olefins include, for example, ethylene, propylene, 1-butene, 1-pentene, 4-methylpentene-1, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, or any combination thereof. Preferably, the α -olefins are ethylene, propene, 1-butene, 4-methylpentene-1, 1-hexene, 1-octene, and combination of any two or more of such α -olefins.

10

POLYMERIZATION

The catalysts of the present invention can be advantageously employed in the polymerization of monomers by the solution or slurry process.

15

The slurry process is employed at temperatures of from 0°C up to a temperature just below the temperature at which the resulting polymer becomes soluble in the inert polymerization medium, preferably at temperatures of from 60°C to 105°C, more preferably from 80°C to 95°C.

20

The solution process is employed at temperatures from the temperature at which the resulting polymer is soluble in the inert reaction medium up to 275°C, preferably at temperatures of from 145°C to 260°C, more preferably from 180°C to 240°C.

25

The polymerization can be employed at pressures of from 1 to 2,000, preferably from 5 to 500, more preferably from 10 to 50, atmospheres.

Molecular weight control agents such as hydrogen can be employed in the manner known to those skilled in the art of polymerizing α -olefins. Usually the greater the amount of hydrogen or terminating agent employed the lower the molecular weight of the resulting polymer. The hydrogen is employed in that quantity which will provide the resulting polymer with the desired molecular weight as indicated by the desired I2 value.

The solution polymerization can be employed in the presence of any suitable inert reaction medium such as, for example, aromatic hydrocarbons, aliphatic hydrocarbons, naphthinic hydrocarbons, or combinations thereof. Particularly suitable inert reaction medium include, for example, hexane, heptane, octane, isooctane, nonane, isononane, decane,

undecane, dodecane, tridecane, tetradecane, cyclohexane, methylcyclohexane, or combinations thereof.

5 The suspension (slurry) polymerization can be employed in the presence of any suitable inert reaction medium such as, for example, aromatic hydrocarbons, aliphatic hydrocarbons, naphthinic hydrocarbons, liquefied α -olefins, liquefied hydrocarbons, or combinations thereof. Particularly suitable inert reaction medium include, for example, isobutane, isopentane, pentane, hexane, heptane, octane, isooctane, nonane, isononane, decane, cyclopentane, cyclohexane, or any combination thereof.

10

The following examples are illustrative of the invention, but are not to be construed as to limiting the scope thereof in any manner.

15 The following components were employed in the examples and comparative experiments.

20 Silica Support #1 was a silica having a mean particle size of 3μ , a surface area of $337\text{ m}^2/\text{g}$, subjected to heating in a fluidized bed under a nitrogen atmosphere at 600°C for 12 hours resulting in a silica support material having a hydroxyl content of 3.2 millimoles/gram.

20

Silica Support #2 was a silica having a mean particle size of 70μ , a surface area of $310\text{ m}^2/\text{g}$, subjected to heating in a fluidized bed under a nitrogen atmosphere at 600°C for 12 hours resulting in a silica support material having a hydroxyl content of 1.9 millimoles/gram

25

Silica Support #3 was a sieve fraction of a silica having a mean particle size of 145μ , a surface area of $310\text{ m}^2/\text{g}$, subjected to heating in a fluidized bed under a nitrogen atmosphere at 800°C for 12 hours resulting in a silica support material having a hydroxyl content of 1.8 millimoles/gram.

30

Silica Support #4 was a sieve fraction of a silica having a mean particle size of 85μ , a surface area of $310\text{ m}^2/\text{g}$, subjected to heating in a fluidized bed under a nitrogen atmosphere at 800°C for 12 hours resulting in a silica support material having a hydroxyl content of 1.8 millimoles/gram.

35

Silica Support #5 was a sieve fraction of a silica having a mean particle size of 40μ , a surface area of $310\text{ m}^2/\text{g}$, subjected to heating in a fluidized bed under a nitrogen atmosphere at 800°C for 12 hours resulting in a silica support material having a hydroxyl content of 1.8 millimoles/gram.

Silica Support #6 was a sieve fraction of a silica having a mean particle size of 3μ , a surface area of $310\text{ m}^2/\text{g}$, subjected to heating in a fluidized bed under a nitrogen atmosphere at 800°C for 12 hours resulting in a silica support material having a hydroxyl content of 1.8 millimoles/gram.

Silica Support #7 was a small size silica having a mean particle size of 3μ , a surface area of $430\text{ m}^2/\text{g}$, subjected to heating in a rotary kiln under a nitrogen atmosphere at 800°C for 5 hours resulting in a silica support material having a hydroxyl content of 2.8 millimoles/gram.

ISOPAR™ E was a fractionated isoparaffinic solvent having a boiling range of 113°C - 143°C available from Exxon Corporation.

Basic physical testing (including melt index, I_2 , I_{10}/I_2 , and density) were performed on each sample using standard ASTM methods as follows:
melt index (I_2) by ASTM D 1238, Condition $190^\circ\text{C}/2.16\text{ kg}$;
melt index (I_{10}) by ASTM D 1238, Condition $190^\circ\text{C}/10\text{ kg}$; melt index (I_{20}) by ASTM D 1238, Condition $190^\circ\text{C}/20\text{ kg}$;
density by ASTM D 792. Melting point was determined using differential scanning calorimetry (DSC).

The molecular weight of the resultant polymers was also determined via gel permeation chromatography (GPC) employing a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10³, 10⁴, 10⁵, and 10⁶), operating at a system temperature of 140°C . The solvent was 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples were prepared for injection. The flow rate was 1.0 milliliter/minute and the injection size was 200 microliters.

The molecular weight determination was deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights were determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968, incorporated herein by reference) to derive the equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , was calculated in the usual manner according to the formula:

$$M_w = \sum w_i \cdot M_i$$

5

where w_i and M_i are the weight fraction and molecular weight respectively of the i th fraction eluting from the GPC column.

The onset of crystallization and crystallization kinetics of each resin was
10 determined by measuring the transmission of plane polarized light through a sample melted at 180°C and allowed to cool to 70°C at a rate of $10^\circ\text{C}/\text{min}$.

The Short Chain Branching Distribution (SCDB) and percent high density fraction of each resin was determined by Analytical Temperature Rising Elution Fractionation (ATREF),
15 as described in USP 4,798,081 and in Journal of Applied Polymer Science, Applied Polymer Science Symposia 45, 25-37 (1990) entitled "Determination of Short-Chain Branching Distributions of Ethylene Copolymers by Automated Analytical Temperature Rising Elution Fractionation (AUTO-ATREF)", by Lonnie G. Hazlett. ATREF separates the polymer according to crystallinity. The experimental procedure for determining short chain branching distribution
20 and high density fraction was as follows:

I. TREF Device Design

A process control gas chromatograph (GC) analyzer was used as the basis of the
25 design and functions as a computer controlled event sequencer and multiple GC oven programmer. The GC uses digital I/O to operate pneumatic solenoids, operate other pneumatic equipment and detect the states of various digital switches. The GC primary components includes two large, forced air, isothermal (135°C) ovens and four smaller, programmable, forced air GC ovens. The GC ovens were operated by vendor supplied software to control the
30 temperature profiles. The software includes other program instructions and consists of a fixed sequence of timed events to provide the necessary control for automation. A five mil sample loop consisting of 1/16 inch ID stainless steel tubing was used to temporarily receive the freshly injected polymer solution. A syringe-pump assembly provides the necessary vacuum to move polymer solution into the sample loop. The syringe pump assembly uses a 5-ml syringe barrel
35 and an air cylinder to drive the plunger. A separate injector head assembly was used to place the needle into the solution of polymer for subsequent removal. This assembly behaves as a valve, since when the needle was down, no flow was possible, and when the valve was up it was

actually part of the flow path. The polymer solutions were introduced to the system via a sample carousel assembly.

Attached to the lower oven were the four programmable GC ovens. In each of
5 these ovens was a small ATREF column constructed of 1/8 inch thin-wall, stainless-steel tubing. These were packed with stainless-steel shot. The total interstitial volume of the columns was 1.5 mL. The solvent and polymer solution was directed, via a heated transfer line, to a single-beam infrared detector set to 3.5 microns. The detector was equipped with a high
10 temperature, flow-through sample cell containing zinc selenide windows spaced to give a 0.1 cm path length. Other detectors including refractive index and viscometers can be used (but are not discussed here). A reservoir for solvent waste was provided after the detector.

In addition to the analyzer computer which operated the system, a separate
personal computer was used as a data system. The software on this latter system includes
15 various data acquisition routines for digitally storing signals from the ATREF instrument and data reductions routines to transform this digitally recorded data into meaningful graphs and reports. Various voltages from the ATREF instrument were measured digitally. These include the infrared detector output, other mass detectors, and thermocouple outputs from each of
the GC ovens.

20 The copolymer solutions were prepared in TCB at about 0.6 percent by weight and heated to 160°C to ensure homogeneity. These solutions were placed into 15 mL vials with open-holed caps fitted with Teflon septa, then placed into the carousel. The carousel was placed in the upper oven and the analyzer computer was then started. The operation was then
25 fully automated for the next 48 hours, provided data collection routines were initiated on the data system and an adequate solvent supply was available.

The operation of the instrument consists of a sequence of four identical program
modules executed on the analyzer computer. The only difference among these modules was
30 the GC oven on which each operates. Each module consists of a sequence of timed events, e.g., VALVE 1 ON, VALVE 5 OFF, TEMPERATURE PROGRAM 1, etc. For simplicity the operation of only one program module (operating on GC oven 1) was described, with the understanding that continuous operations requires the use of all four program modules.

35 It will be assumed that GC oven 1, initially at 24°C, contains a previously precipitated copolymer and that the oven was now ready for elution. This means the instrument has been running for some time and the precipitated polymer in the column was from a previous injection. Valve 1, valve 5, and valves 7 through 10 were closed. Valve 4 and

valve 6 were open. The flow (1.5 mL/min) was bypassing the upper oven and all of the GC ovens. The detector was in a baseline condition and only pure TCB was moving through the system.

5 The first step in each program module was to notify the data system via a set of contact closures that an elution step was being initiated. The next step was to open valve 7 above GC oven 1 and close valve 6. As the fresh solvent enters GC oven 1, it displaces the solvent left in the column during the precipitation of the polymer solution. In nearly all cases there was a fraction of the polymer which does not precipitate, even at 24°C. As the displaced
10 solvent exits the oven it was directed into the IR detector. After the initial column contents were eluted and the IR detector has returned to a baseline condition, GC oven 1 was subjected to a temperature program of +1.5°C/min. A continuous response was produced in the IR which was proportional to the concentration of the eluting polymer in solution. This detector response and the response from an internal thermocouple were recorded on the data system as
15 a function of time.

 After GC oven 1 has reached 122°C, the elution step was assumed to be complete. The solvent flow was maintained as above while in the upper oven, valve 2 was opened, and valve 3 was closed. The carousel was advanced one position. The syringe needle within the
20 injector head was lowered. The syringe pump was pulled down and polymer solution was pulled into the sample loop. The sample loop was sufficiently large to prevent any of the solution from entering the syringe pump mechanism. A 5 minute delay was included to ensure that solutions with a range of viscosities will have time to fill the loop.

25 The next steps were to load the column in GC oven 1 and reset the injector components to their initial states. Valve 2 was closed, the needle was raised, valve 3 was opened, and the syringe pump was forced upwards, expelling excess TCB to waste. Valve 1 and valve 5 were opened and valve 4 was closed. The polymer solutions located in the sample loop moves under nearly plug flow conditions toward GC oven 1, maintained at 122°C. At the
30 approximate time that the moving plug of polymer solution was centered over the column in GC oven 1, valve 6 was opened and valve 7 was closed. The portion of the moving 5-mL column will now be isolated from the flow and remain behind as the excess solution was flushed out of the system. This condition was maintained for 30 minutes to ensure that the upper ovens were well flushed with fresh solvent.

35 Three temperature programs for GC oven 1 were initiated. First was a quick cool from 122°C to 106°C at -10°C/min. Next, a temperature program was started from 106°C at -0.1°C/min. At this rate the total cool down would require in excess of 13 hours to complete.

This time was shortened somewhat by the final temperature program of $-0.3^{\circ}\text{C}/\text{min}$, which starts when the oven temperature reaches 50°C . The total cool down time requires about 10.5 hours; and since each of the program modules was only a little over 3 hours, the last temperature program referred to above ($-0.3^{\circ}\text{C}/\text{min}$.) actually resides in the program module
5 operating on GC oven 4. Near the end of each program module the valves were returned to the initial conditions described at the beginning of this section in preparation for the next module. The subsequent modules were identical except they operate on successive GC ovens.

The digitized ATREF data were a record of the IR detector response and the
10 column temperature as a function of time. The data reduction routine includes baseline subtraction, conversion to the temperature domain, smoothing, normalization and plotting the data.

The bimodality of the distributions was characterized by the weight fraction of
15 the highest temperature peak. This fraction was referred to as the high-density fraction, since it contains little or no short-chain branching. The remaining fraction was therefore logically referred to as the SCB fraction, since it represents the fraction which contains nearly all the short-chain branching inherent to the copolymer.

20 The advantage of the IR detector tuned to the carbon stretching frequency was that the detector response was more nearly uniform, so that low levels of additives do not appreciable interfere with the measurement of the "purge" peak. The fraction of "purge" was represented in the rectangular area near 25°C . The copolymer in this fraction contains very high levels of SCB.

25 The copolymers used in making the novel films described herein have broad short chain branching distributions. This means that the copolymers contain comparatively larger high density and purge fractions and comparatively less intermediately branched material than less preferred copolymers. A copolymer having a SCBD with greater than about 17 percent
30 high density fraction was especially preferred, and a SCBD with at least about 20 percent high density fraction was most preferred.

D Branching Content Determination

Branching content (i.e., degree of branching) was calculated from $\text{CH}_3/1000\text{C}$
35 (methyls/1000 carbons) determination according to ASTM method D2238-68. A Beckman 4260 infrared spectrophotometer was employed, using films of approximately 0.15 mm thickness. A correction for chain end methyl groups was necessary for accurately determining weight

percent comonomer (e.g., 1-octene) incorporation. The correction was done according to the following equation:

$$5 \quad \text{Corrected CH}_3/1000\text{C} = \frac{\text{Uncorrected CH}_3/1000\text{C} + \text{Vinyl} - 28000}{1000\text{C} \quad \text{Mn}}$$

Comonomer incorporation can be determined from the following equation:

$$\text{Wt. \% octene} = \frac{(\text{Molecular Weight of 1-octene}) (\text{Corrected CH}_3/1000\text{C}) (100)}{14000 + 84 (\text{corrected CH}_3/1000\text{C})}$$

15 The width of the SCBD was described using the z value, the calculation of which for a fraction of a whole polymer crystallized at its crystallization temperature T_c may be obtained by determining the fraction of methyls/1000 carbons by ^{13}C NMR (corrected for chain ends i.e. molecular weight) and calculating the mole fraction of the average sequence length of methylene units as shown below where m was the carbon number of the comonomer, M_n 20 was the number average molecular weight and x was number of methyls/1000 carbons (corrected):

$$z = \{1 - (x(m-1)/1000 + 28/M_n)\} 1000 / (x + 1)$$

25 If this calculation was repeated for a fraction across the T_c range of the whole polymer, the new distribution reflects the weight fraction of polymer (from ATREF) as a function of average crystallizable segment mole fraction. Two moments can then be defined:

$$30 \quad z_0 = (E_{w_i}/z_i) - 1$$

and

$$z_1 = E_{w_i} \times z$$

35 where w_i was the weight percent of the i th fraction and z_i was the value of z calculated from the observed T_c for the i th fraction. For the polymers of the current invention, the weight fraction at each T_c was determined by ATREF and the corrected methyls per 1000 carbons for each T_c

was determined using a previously determined calibration curve of Tc vs methyls/1000 carbons obtained from fractions of the same product type.

Morphological analysis was carried out using a Nikon Polarizing Microscope (Optiphot-Pol) equipped with an analyzer and a polarizer. Sample preparation involved melting the sample at 180°C and allowed to cool to 70°C at a rate of 10°C/min. When cool the sample was placed on a microscope slide and the pictures were taken using a 35 mm camera which was attached to the phototube. The filter holder was positioned directly next to the light source to avoid any flare of false images from the filter surface while taking pictures. Photographs were taken using objective lenses which resulted in a magnification of 200X.

Polymerization (Solution Conditions)

A stirred, one-gallon (3.79L) autoclave reactor was charged with two liters of ISOPAR™ E and the required amount of the alpha-olefin comonomer, octene-1, in an amount such that its molar concentration in the reactor was 0.99M before heating to the desired temperature. The required amount of hydrogen, 2 psig (13.8 kPa), was then added to the reactor followed by ethylene sufficient to bring the total pressure to 450 psig (3,103 kPa). An amount of the activated catalyst was injected into the reactor. The reactor temperature and pressure were maintained constant at the initial pressure and temperature, as indicated, by continually feeding ethylene during the polymerization run and cooling the reactor as necessary. After a 10 minute reaction time (unless otherwise indicated), the ethylene was shut off and the hot solution transferred into a nitrogen-purged resin kettle. After drying, the samples were then weighed to determine catalyst efficiencies followed by melt flow and density measurements via standard procedures.

Polymerization (Slurry Conditions)

A stirred, 1.4 liter autoclave reactor was charged with 700 mL of ISOPAR™ E before heating to the desired temperature. The vapor space was swept with hydrogen and then hydrogen was added to the reactor until the desired partial pressure was reached. This was followed by ethylene sufficient to bring the total pressure to 175 psig (1,207 kPa). An amount of the activated catalyst as described under preparation of activated catalyst was injected into the reactor. The reactor temperature and pressure were maintained constant at the initial pressure and temperature by continually feeding ethylene during the polymerization run and cooling the reactor as necessary. After a 45 minute reaction time (unless otherwise indicated), the ethylene was shut off and the polymer slurry transferred into a nitrogen-purged

resin kettle. After drying, the samples were then weighed to determine catalyst efficiencies followed by melt flow and density measurements.

EXAMPLE 1

5

A. Preparation of Transition Metal Catalyst Component

To 1 g of Silica Support #1 slurried in 50 ml of ISOPAR™ E was added the required amount of butyloctylmagnesium ethoxide (BOMAG-O from Schering A.G.). The resulting slurry was stirred for 1 hour after which an amount of titanium tetrachloride (TiCl₄) was added. The slurry rapidly darkens to a deep brown color and was stirred for a further two hours. An aliquot of a solution of 25 percent ethylaluminum dichloride was then added and the final mixture stirred for 17 hours. The complete mixtures prepared in this manner were used without further isolation or washing. The catalysts have the atomic ratios as indicated in Table I.

15

B. Preparation of Activated Catalyst

An activated catalyst was prepared by slurrying 4 mL of the transition metal catalyst component in 40 mL of ISOPAR™ E in a 100 mL septum-capped bottle in a glove box. To this mixture was added the required amount of 0.15 M solution of triethylaluminum in hexane as a cocatalyst or activator. The resulting slurry was made up to 50 mL total volume with ISOPAR™ E and the mixture injected into the batch reactor to effect the polymerization. The atomic ratio of Al from the cocatalyst to titanium was provided in Table I.

25

C. Polymerization (Solution Conditions)

The polymerization procedure under solution conditions was employed at a polymerization temperature of 185°C. The catalyst efficiency was provided in Table I.

30

D. (Comparative)

A catalyst was prepared as described in U.S. Patent 4,562,169 in the following manner:

35

Davison Silica Gel, Grade 952, was dehydroxylated by fluidizing with nitrogen and heating at 800°C for 12 hours and cooled to room temperature under nitrogen

10 grams of the activated silica was slurried in 100 mL of anhydrous degassed hexane, brought to a reflux temperature of 60°C and 7 mL of a 2.6 M solution of ethylmagnesium chloride in tetrahydrofuran (THF) added slowly followed by further refluxing for 120 minutes. The solvents were removed by distillation and the silica dried at 80°C under a nitrogen purge.

This product was slurried with a premixed solution of 6 mL of $TiCl_4$ dissolved in 100 mL of Isopar™ E and the slurry stirred at 50°C for two hours. This mixture was allowed to cool to room temperature and the solids washed twice with 100 mL portions of Isopar™ E and twice with 100 mL portions of hexane and dried under a nitrogen purge to yield a tan colored free-flowing powder. Analysis of the powder indicates that it contains 1.3 mmol/g Mg/g catalyst, 0.9 mmol Ti/g catalyst and 4.5 mmol Cl/g catalyst. The catalyst was then combined with triethylaluminum (TEA) activator (cocatalyst) by slurrying 2 g of the dry catalyst in 40 ml of Isopar™ E in a 4 oz (118.3 mL) septum capped bottle in a glove box. A 2 mL aliquot of this solution was transferred to a second bottle to which was added the required amount of a 0.15 M solution of triethylaluminum in hexane followed by an additional 20 mL of Isopar™ E. The required amount of this slurry was then injected into a batch reactor to effect the polymerization under solution conditions at 175°C as described earlier. The catalyst efficiency and product data are shown in Table I.

20

25

30

35

Table I

Run No.	Catalyst Source	mmol Mg	mmol Ti	mmol Al	mmol Cl	Atomic Ratio Mg/Al ^a /Cl/Ti	Atomic Ratio of Al ^b /Ti	Efficiency (Kg Polymer per gram Ti or Cl)	
								Ti	Cl
A	Ex 1-B	1.4	0.4	4.5	10.6	3.5/11.3/26.5/1	11/1	478	24
B	Ex 1-B	1.9	0.4	4.5	10.6	4.8/11.3/26.5/1	6/1	627	28
C	Ex 1-B	1.8	0.2	3.5	9.4	3.0/5.8/15.7/1	5/1	413	27
D	Ex 1-D	1.3	0.9	---	4.5	-----	5/1	30	8

- a Aluminum from transition metal catalyst component.
b Aluminum from cocatalyst.

EXAMPLE 2

A. Preparation of Transition Metal Catalyst Component

To a 1 g sample of the support designated in Table II slurried in 50 mL of ISOPAR™ E was added 2.0 mmol of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc.). The mixture was stirred for one hour and treated sequentially with 1.0 mmol TiCl_4 and 1.0 mmol $\text{V}(\text{O})\text{Cl}_3$ as a neat mixture and 6.0 mmol of ethylaluminum dichloride (4.0 mL of a 1.5 M solution in hexane). The mixture was diluted to 100 mL total volume and then stirred for 24 hours. The atomic ratios of the components in the transition metal complex were Mg/Al/Cl/Ti/V was 2/6/19/1/1. The catalyst components were activated (use of cocatalyst) according to the procedure described in Example 1 employing Al (activator)/Ti ratio of 8/1.

B. Polymerization

The polymerizations were conducted under solution process conditions at 185°C. The results of the polymerization reactions are shown in Table II.

Table II. Effect of Silica Particle Size on Solution Polymerizations

Run No	Support		Density g/cc	I_2	Efficiency (Kg Polymer per gram Ti or Cl)	
	No.	Size μ			Ti	Cl
A*	3	145	0.9080	1.16	49	30
B*	5	40	0.9119	1.05	499	35
C	6	3	0.9159	1.13	842	60

* Not an example of the present invention.

EXAMPLE 3

A. Preparation of Transition Metal Catalyst Component

To 1 g of the indicated silica support of different mean particle sizes slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred for 1 hour after which 0.20 mmol of titanium tetraisopropoxide was added. The slurry was stirred for a further two hours. An aliquot of a

solution of 25 percent ethylaluminum dichloride (4.0 mmol Al) was then added and the final mixture stirred for 17 hours. The complete mixtures prepared in this manner were used without further isolation or washing. The atomic ratios of Mg/Al/Cl/Ti were 10/20/40/1

5 The catalysts were activated with triisobutylaluminum at an atomic ratio of Al/Ti of 100/1 by the procedure described in Example 1B

B. Polymerization

10 The polymerizations were conducted under slurry conditions using a hydrogen to ethylene ratio of 1:1 and a reactor temperature of 85°C. The results of the polymerization reactions are shown in Table III.

Table III. Effect of Silica Particle Size on Slurry Polymerizations

Run No.	Catalyst Support		Atomic Ratios			I ₂	I ₂ /I ₂	Efficiency (Kg Polymer per gram of Ti or Cl)	
	#	Size (μ)	Transition Metal Catalyst Component		Cocat. Al/Ti			Ti	Cl
			Mg/Al/Cl/Ti	Si/Mg					
A*	3	145	10/20/40/1	8.3	100:1	0.40	42.8	531	18
B*	4	85	10/20/40/1	8.3	100:1	0.33	34.7	727	24
C*	5	40	10/20/40/1	8.3	100:1	0.48	36.9	575	19
D	6	3	10/20/40/1	8.3	100:1	0.37	38.7	1,500	51
E	7	3	10/20/40/1	8.3	100:1	0.30	34.2	1,510	51

* Not an example of the present invention.

EXAMPLE 4

A. Preparation of Transition Metal Catalyst Component

30

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred for 1 hour after which 0.20 mmol of titanium tetrachloride (TiCl₄) was added. The slurry rapidly darkens to a deep brown color and was stirred for a further two hours. An aliquot of a solution containing an alkylaluminum chloride (3.5 mmol Al) was then added and the final mixture stirred for 17 hours. The complete mixtures prepared in this manner were used without further isolation or washing.

35

The catalysts were activated with triisobutylaluminum at a ratio of Al/Ti of 100/1 employing the procedure of Example 1B.

5 B. Polymerization

The polymerizations were conducted under slurry conditions using a hydrogen to ethylene ratio of 1:1, a reactor temperature of 85°C and a polymerization time of one hour. The results of the polymerization reactions are shown in Table IV.

10

Table IV. Effect of different Alkylaluminum Halides

Run No.	Aluminum Source	Atomic Ratios			Efficiency (Kg PE per gram of Ti or Cl)		I ₂	I ₂ /I ₂
		Catalyst		Cocat. Al/Ti	Ti	Cl		
		Mg/Al/Cl/Ti	Si/Mg					
A	EtAlCl ₂ ^a	10/17.5/39/1	8.3	100/1	1,150	40	0.71	24.7
B	Et ₃ Al ₂ Cl ₃ ^b	10/17.5/30.3/1	8.3	100/1	986	44	0.80	31.8
C	iBuAlCl ₂ ^c	10/17.5/39/1	8.3	100/1	1,010	38	0.69	30.0

20

- a Ethylaluminum dichloride.
 b Ethylaluminum sesquichloride.
 c Isobutylaluminum dichloride

25 EXAMPLE 5

A. Preparation of Transition Metal Catalyst Component

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred for one hour after which an amount of titanium tetraisopropoxide was added. The slurry was stirred for a further two hours. An aliquot of a solution of 25 percent ethylaluminum dichloride in hexane was then added and the final mixture was stirred for 17 hours. The complete mixtures prepared in this manner were used without further isolation or washing.

35

V.

The catalysts were activated with triisobutylaluminum at the ratio given in Table

B. Polymerization (Slurry Conditions)

The polymerization was conducted under slurry polymerization conditions employing a temperature of 85°C, a hydrogen to ethylene ratio of 1:1 and a polymerization
5 time of one hour.

The results are shown in Table V

Table V. Effect of Varying Amount of Titanium and Cocatalyst

Run No.	Atomic Ratios			Efficiency (Kg PE per gram of Ti or Cl)	
	Catalyst		Cocat. Al/Ti	Ti	Cl
	Mg/Al/Cl/Ti	Si/Mg			
A	6.7/15/30/1	8.3/1	25/1	1,150	52
B	6.7/11 7/23.3/1	8.3/1	100/1	1,100	64
C	10/35/70/1	8.3/1	100/1	2,140	41

EXAMPLE 6

20

A. Preparation of Transition Metal Catalyst Component

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred
25 for 1 hour after 0.20 mmol of titanium tetraisopropoxide ($Ti(O-iC_3H_7)_4$) was added. The slurry was stirred for a further two hours. An aliquot of a solution of 25 percent ethylaluminum dichloride (4.5 mmol) was then added and the final mixture stirred for 17 hours. The complete mixtures prepared in this manner were used without further isolation or washing. The atomic ratio for the catalysts are given in Table VI.

30

The catalysts were activated with triisobutylaluminum at an Al/Ti ratio of 200:1

B. Polymerization (Slurry Conditions)

The polymerization was conducted under slurry polymerization conditions
35 employing a temperature of 85°C, a hydrogen to ethylene ratio of as indicated in the Table, a pressure of 170 psi (1,172 kPa), and a polymerization time of one hour. Various solvents were employed as the polymerization medium. The results are given in Table VI

Table VI. Use of Different Solvents as a Polymerization Medium and different Hydrogen to Ethylene Ratios.

Run No.	Solvent	Atomic Ratios			Ratio of H ₂ to C ₂ H ₄	I ₂	I ₂ /I ₂	Efficiency (Kg Polymer per gram of Ti or Cl)	
		Catalyst		Cocat. Al/Ti				Ti	Cl
		Mg/Al/Cl/Ti	Si/Mg						
A	n-C ₆ H ₁₄	10/22 5/45/1	8.3/1	200/1	0.36	0.19	39.5	1,020	31
B	i-C ₅ H ₁₂	10/22 5/45/1	8.3/1	200/1	3.0	0.67	38.5	750	22

EXAMPLE 7

A. Preparation of Transition Metal Catalyst Component Containing Vanadium

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of
5 butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred
for one hour after which 0.40 mmol of titanium tetrachloride (TiCl_4) was added. The slurry
rapidly darkens to a deep brown color and was stirred for a further two hours. An aliquot of a
solution of ethylaluminum dichloride (3.5 mmol Al) was then added and the final mixture
10 stirred for 17 hours. The mixture was treated with 0.40 mmol of vanadium trichloride oxide
(VOCl_3) and then stirred for 4 hours. The Mg/Al/Cl/V/Ti atomic ratios of the catalyst was
5/8.8/20.3/1/1. The Si/Mg atomic ratio of the catalyst was 8.3/1.

The catalyst was activated with triisobutylaluminum at an Al/Ti atomic ratio of
100:1

15

B. Polymerization (Slurry Conditions)

The slurry polymerization conditions were employed. The polymerization
temperature was 85°C, the hydrogen to ethylene ratio was 2:1, and the polymerization time
20 was one hour.

The polymerization efficiency based on titanium was found to be 952 Kg PE/g Ti
and the polymerization efficiency based on chloride was 52 Kg PE/g Cl and the polymerization
efficiency based on titanium plus vanadium was 476 Kg PE/g Ti + V.

25 EXAMPLE 8

A. Preparation of Transition Metal Catalyst Component Containing Vanadium

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of
butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc.) The resulting slurry was stirred
30 for one hour after which 1.80 mmol of titanium tetrachloride (TiCl_4) was added. The slurry
rapidly darkened to a deep brown color and was stirred for a further two hours. An aliquot of
a solution of ethylaluminum dichloride (3.5 mmol Al) was then added and the final mixture
stirred for 17 hours. The mixture was treated with 0.40 mmol of vanadium trichloride oxide
(VOCl_3) and then stirred for 4 hours. The Mg/Al/Cl/V/Ti atomic ratios of the catalyst was
35 1.1/1.9/12.3/0.2/1. The Si/Mg atomic ratio of the catalyst was 8.3/1.

The catalyst was activated with triisobutylaluminum at an atomic ratio of Al/Ti of
100/1

B. Polymerization (Slurry Conditions)

The slurry polymerization procedure was employed using a hydrogen to ethylene
5 mole ratio of 1 to 1, a polymerization temperature of 85°C, and a polymerization time of one
hour.

The efficiency of the catalyst based on titanium was 571 Kg PE/g Ti/hour and the
efficiency based on chloride was 90 Kg PE/g Cl and the efficiency based on titanium plus
10 vanadium was 285 Kg/g of Ti + V/hour.

EXAMPLE 9

A. Preparation of Transition Metal Catalyst Component Containing Vanadium

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of
15 butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred
for 1 hour after which 1.00 mmol of titanium tetrachloride (TiCl₄) was added. An aliquot of a
solution of ethylaluminum dichloride (6.0 mmol Al) was then added and the final mixture
stirred for 17 hours. The mixture was treated with 1.00 mmol of vanadium trichloride oxide
20 (VOCl₃) and then stirred for 4 hours. The complete mixtures prepared in this manner were used
without further isolation or washing. The Mg/Al/Cl/V/Ti atomic ratios of the catalyst was
2/6/19/1/1. The Si/Mg atomic ratio of the catalyst was 8.3/1.

The catalysts were activated with the cocatalyst designated in Table VII.

25

B. Polymerization (Slurry Conditions)

The slurry polymerization procedure was employed at a temperature of 85°C a
hydrogen to ethylene ratio of 1:1, and a polymerization time of one hour

30

The catalyst efficiency and properties of the resulting polymer are shown in Table

VII

35

Table VII. Use of Varying Amounts of Vanadium

Run No.	Cat. No.	Bu ₃ Al TO Ti Ratio	Efficiency (Kg PE per gram of Ti or Cl)			I ₂	I ₂₀ /I ₂
			Ti	Cl	Ti + V		
A	9A	100	433	31	216	0.12	60.0
B	9B	200	433	31	216	0.12	60.3
C	9C	50	325	23	163	0.09	57.8

This Example 9 shows that high I₂₀/I₂ ratios can be achieved with the vanadium containing catalysts in slurry polymerizations. These high I₂₀/I₂ ratios were indicative of a broad molecular weight distribution.

EXAMPLE 10

A Preparation of Transition Metal Catalyst Component

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 2.0 mmol of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred for one hour after which titanium tetraisopropoxide was added in the indicated quantities. The slurry was stirred for a further two hours. An aliquot of a solution of 25 percent ethylaluminum dichloride in hexane was then added and the final mixture stirred for 17 hours. The atomic ratios of Mg/Al/Cl/Ti for these catalysts were as follows:

Run A = 7.5/15/30/1

Run B = 3.8/8.8/17.5/1

The atomic ratios of Si/Mg for these catalysts were as follows:

Run A = 8.3/1

Run B = 8.3/1

The catalysts prepared in this manner were used without further isolation or washing

The catalysts were activated with triethylaluminum at atomic ratios of Al/Ti of 8/1 and 6/1

B. Polymerization (Solution Conditions)

The catalysts were used to polymerize ethylene using the solution polymerization procedure employing a polymerization temperature of 185°C, and a polymerization time of one hour.

The results were given in Table VIII

Table VIII

Run No.	Catalyst (millimoles)		Cocat. Atomic Ratio Al/Ti	Efficiency (Kg PE per g Ti or Cl)	
	Ti	Al		Ti	Cl
A	0.20	3.0	8	773	35
B	0.40	3.5	6	641	50

EXAMPLE 11

A. Preparation of Catalyst

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added the required amount of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred for one hour after which titanium tetrachloride (TiCl₄) was added. An aliquot of a solution of ethylaluminum dichloride (EADC) was then added and the slurry stirred for 17 hours. The mixture was treated with vanadium tetrachloride (VCl₄) and then stirred for 4 hours. The complete mixtures prepared in this manner were used without further isolation or washing. The composition of these catalysts are given in Table IX. The atomic ratios are given in Table IX.

B. Activation and Polymerization

After activating the catalysts prepared above with triethylaluminum in the indicated amounts, polymerizations were conducted under solution polymerization conditions at a polymerization temperature of 185°C and a polymerization time of ten minutes.

The results are given in Table IX

Table IX

Run No	mmol BEMB	mmol TiCl ₄	mmol VCl ₄	mmol EADC	Atomic Ratios			Density g/cm ³	l ₂	Catalyst Efficiency Kg PE/g Ti or Cl	
					Catalyst		Cocat Al/Ti			Ti	Cl
					Mg/Al/Cl/V/Ti	Si/Mg					
	1.2	0.2	0.2	1.5	6/7.5/23/1/1	14/1	9.4	0.9334	3.45	552	32
B	1.2	0.6	0.2	1.5	2/2.5/10/0.33/1	14/1	5.2	0.9314	3.74	593	77
C	1.5	0.4	0.4	2.5	3.8/6.3/20.5/1/1	17/1	4.7	0.9250	1.24	1,096	72
D	1.8	0.6	0.6	3.5	3/6/20/1/1	21/1	6.7	0.9241	1.81	1,021	70
E	1.2	0.6	0.6	3.5	2/6/20/1/1	14/1	8.3	0.9228	1.16	958	66
F	1.2	1.0	1.0	3.5	1.2/3.5/15/1/1	14/1	8.3	0.9285	1.21	1,157	104
G	1.2	1.2	1.2	3.5	1/3/14/1/1	14/1	8.3	0.9232	1.84	807	79
H	1.2	0.6	0.2	3.5	2/7/19/0.3/1	14/1	8.3	0.9226	1.47	1,002	80

EXAMPLE 12

A. Preparation of Transition Metal Catalyst Component

To 1 g of Silica Support #7 slurried in 50 ml of ISOPAR™ E was added 1.2 mmol
5 of butylethylmagnesium butoxide (BEMB from Texas Alkyls Inc). The resulting slurry was stirred
for one hour after which 0.60 mmol of titanium tetrachloride (TiCl_4) was added. The slurry
rapidly darkens to a deep brown color and was stirred for a further two hours. An aliquot of a
solution of ethylaluminum dichloride (3.5 mmol Al) was then added and the final mixture was
stirred for 17 hours. The mixture was treated with 0.60 mmol of vanadium trichloride oxide
10 (VOCl_3) and then stirred for 4 hours.

The catalyst has the following ratios:

Mg/Al/Cl/V/Ti of 2/5.8/18/1/1

Si/Mg of 13.9/1

15 B. Activation and Polymerization Under Solution Conditions

After activating the catalyst with triethylaluminum (Al/Ti = 5/1) the
polymerization was conducted using the solution polymerization procedure.

20 The polymer product has a density of 0.9239 g/cm³ and an I2 value of 2.36 and
was produced at an efficiency of 790 Kg PE/g Ti and 57 Kg PE/g Cl.

EXAMPLE 13

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A. Preparation of Transition Metal Catalyst Component

To 1 gram of Silica Support #7 in ISOPAR™ E was added 1.2 mmol of
butylethylmagnesium butoxide. After stirring the mixture for two hours, 3.5 mmol of
30 ethylaluminum dichloride was added and the mixture was stirred for 17 hours. To this mixture
was then added a 1:1 molar mixture of TiCl_4 and VOCl_3 (6 mmol Ti/6 mmol V). This mixture
was stirred for 8 hours.

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The catalyst has the following ratios:

Mg/Al/Cl/V/Ti of 2/5.8/18/1/1; and

Si/Mg of 13.9/1.

5

B. Activation of Catalyst and Polymerization Under Solution Conditions

After activating the catalyst with triethylaluminum (Al/Ti = 5/1), the polymerization was conducted using the solution polymerization procedure.

10

The polymer product has an efficiency of 742 Kg PE/g Ti and 54 Kg PE/g Cl.

EXAMPLE 14

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A. Preparation of Transition Metal Catalyst Component

To 1 g of Silica Support Sample #7 slurried in ISOPAR™ E was added 2.0 mmol of butylethylmagnesium butoxide, 1.8 mmol titanium tetrachloride and 1.8 mmole of vanadium trichloride oxide and the mixture was stirred for 4 hours. The mixture was then treated with 6.5 mmol of ethylaluminum dichloride and the slurry stirred for 24 hours. The atomic ratios of Mg/Al/Cl/Ti/V for this catalyst were 1.1/3.6/13/1/1.

20

B. Activation of Catalyst and Polymerization

An aliquot of the catalyst was diluted and activated according to Example 1B using a triethylaluminum to titanium ratio of 8.5:1. The polymerization was carried out according to the procedure for solution process polymerizations at the temperatures shown in Table X.

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A. Preparation of Transition Metal Catalyst Component

Table X

Run No.	Run Temp. °C	Density g/cc	I ₂	Efficiency (Kg PE per gram of Ti or Cl)	
				Ti	Cl
A	185	0.9251	0.81	945	98
B	215	0.9259	0.71	319	33

To 1 g of Silica Support #7 slurried in Isopar™ E was added 2.0 mmol of magnesium bis(2,6-dimethylcyclohexoxide), 0.2 mmol titanium tetrachloride and the mixture was stirred for 1 hour. The mixture was then treated with 5.5 mmol of ethylaluminum dichloride and the slurry stirred for 24 hours. The atomic ratio of Mg/Al/Cl/Ti for this catalyst was 10/27.5/59/1.

20

B. Activation of Catalyst and Polymerization

An aliquot of the catalyst was diluted and activated according to Example 1B using a triethylaluminum to titanium ratio of 12:1. The polymerization was carried out according to the procedure for solution process polymerizations at 185°C. The polymer product had a density of 0.9332 g/cm³ and an I₂ value of 2.42 g/10 min, an I₁₀/I₂ ratio of 8.0 and was produced at an efficiency of 149 Kg PE/g Ti and 3.4 Kg PE/g Cl

EXAMPLES 16-32

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Preparation of Catalyst for Example 16.

A 410 g sample of Davison SYLOID™ 245 silica was heated at 800°C in a rotary kiln under nitrogen and then slurried in 3 gallons (11.35 L) of ISOPAR™ E. This silica support has a surface area of 401 m²/gram, and a particle size of 3 microns. A 12 gallon (45.4 L) vessel was charged with 20 lbs (9.07 kg) of Isopar E followed by the silica slurry.

After silica addition, 1.86 kg of butylethylmagnesium butoxide (BEMB, Texas Alkyls, 0.97 wt percent Mg in heptane) was then added. The slurry was stirred for 2 hours followed by the addition of 157 mL of an equimolar mixture of titanium tetrachloride and vanadium oxytrichloride (VTi mix, Akzo Chemical) was added. After the addition, the slurry
5 was stirred for one hour and then 4.8 kg of ethylaluminum dichloride (EADC, Texas Alkyls, 2.15 wt percent Al in hexane) was then added.

The catalysts employed in Examples 17 to 32 were prepared in a manner similar to that described above for Example 16.

10

Comparative Example A*

A 445 g sample of Davison SYLOID™ 245 silica was heated at 800°C in a rotary kiln under nitrogen and then slurried in 3 gallons (11.35 L) of ISOPAR™ E. This silica support has a
15 surface area of 391 m²/gram, and a particle size of 3 microns. A 12 gallon (45.4 L) vessel was charged with 20 lbs (9.07 kg) of Isopar E followed by the silica slurry.

After silica addition, 2.01 kg of butylethylmagnesium butoxide (BEMB, Texas
20 Alkyls, 0.97 wt percent Mg in heptane) was then added. The slurry was stirred for 2 hours followed by the addition of 19.5 mL of neat titanium tetrachloride (TiCl₄, Aldrich Chemicals) was added. After the Ti addition, the slurry was stirred for one hour and then 2.38 kg of ethylaluminum dichloride (EADC, Texas Alkyls, 2.15 wt percent Al in hexane) was then added.

25 The dilute catalyst was then injected into the reactor of a continuous solution process pilot plant. Reactor temperature was controlled by the catalyst injection rate. The triethylaluminum (TEA) sidestream co-catalyst was injected into the reactor entry line. Reactor temperature and TEA/Ti ratios were varied to optimize catalyst efficiency. A standard additive package of 1250 ppm calcium stearate, 200 ppm IRGANOX™ 1010, and 1200 ppm IRGAFOS™
30 168 in the polymer was injected as a slurry after the reactor.

Film Manufacture

Film was made using the copolymers of the present invention by fabricating on a
35 three layer (A/B/C) co-extrusion cast film line. For examples 16-21 and Comparative Example A*, the same copolymer was simultaneously extruded through all three extruders, making a three layer film structure having the same copolymer in each layer. The line speed was

maintained at approximately 800 feet/minute at a total gauge of about 0.8 mils using a 30 inch manual adjust die. The draw distance from the die to the primary chill roll for these experiments was about 5 inches. For Examples 16-21 and Comparative Examples A* and B*, the three extruders were operated as follows:

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Table XI

Extruder	diameter (inches)	RPM	Throughput (lbs/hour)	percent of total structure	Melt Temp (°F)
A	2.5	27.4	52.5	15	549
B	3.5	48.4	245	70	552
C	2	44.8	52.5	15	544

10

Film performance was evaluated using a Lantach SHS rotary wrapping machine. The film was placed on the pallet wrapper and stretched wrapped beginning at 0 percent elongation. The film elongation was gradually increased until the film cannot be stretched any farther without breaking. The final elongation beyond which the film cannot be stretched wrapped was called the ultimate stretch point or ultimate stretchability for that film. Films which have the highest ultimate stretchability have the most preferred performance.

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The puncture resistance of the film was measured by cutting each sample to a size of 6 inches (15.2 cm) by 6 inches from the film and testing the film samples on an Instron Tensile Tester. The Instron was equipped with a 100 pound load cell and was operated at a cross-head speed and chart speed of 10 inches/minute. The load range was up to 50 percent. Each sample was held in place by a clamping unit which has a 4 inch (10.2 cm) diameter circular interior. The thickness (T) of the center of each film sample was measured and recorded. Each sample was secured into the clamping unit. A 0.5 inch diameter (1.3 cm) ball attached to the end of a rod was used as the puncturing mechanism. The puncture probe (attached to the upper cross-head) was lowered onto and into the film until the film punctures, or the cross-head has traveled 8 inches, or 40 pounds force was reached. At puncture, the energy (E) required to break the film was recorded. The puncture resistance (PR) was then calculated by the following equation:

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$$PR = E/(12)*(T)*(A),$$

where: PR was puncture resistance in foot-pounds/in³,
E was the puncture energy in inch-pounds,
12 inches/foot was a conversion factor,
T was the film thickness in inches, and
A was the area of the clamped film specimen sample (12.56 in² for these samples).

Six samples were tested for each film and the results were averaged.

EXAMPLES 16-21

Examples 16-21 in Table XIA summarizes the catalyst formulation for each example. The data in Table XIB summarizes the copolymer product data observed using the catalysts and process of the current invention at a constant reactor temperature of 195°C while targeting a 2.3 melt index, 0.917 g/cm³ density product using octene as comonomer, as well as properties of cast film made from the copolymers. The comonomer and hydrogen were adjusted to achieve the target density and melt index, respectively. Broad SCBD copolymers contain more comonomer than narrow SCBD copolymers.

Copolymers shown in Table XIB, produced from the catalysts described in Table XIA, clearly demonstrate an increase in z-ratio and decrease in crystallization onset temperature, as the Mg:Ti ratio of the catalyst increases.

Table XIB also demonstrates that films made from the copolymers made using the novel catalysts and process of the present invention have excellent ultimate stretchability and good puncture resistance, especially when the copolymers have a percent high density greater than about 17 percent and a M_w/M_n ratio of less than about 3.6, especially less than about 3.3."

Comparative Experiment A*, when compared to Examples 16-21, illustrates the importance of the presence of vanadium in the catalyst on z ratio, I10/I2 and percent stretch. Comparative Example B* was an ethylene/1-hexene gas phase copolymer sold into the stretch

film market for use in pallet wrapping and was produced by Exxon Chemical (known as Exxon 3002.37). Comparing the film made from Examples 16-18 with films made from Examples 19-21 and from comparative examples A* and B* shows that a copolymer having the combination of narrow molecular weight distribution (i.e., a low Mw/Mn) and broad SCBD (high percent high density fraction), when made into cast film, has both high ultimate stretchability and good puncture resistance.

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Table XIA
Catalyst Properties**

Ex. or C.E. No.	Surface Area m ² /gram	Catalyst Composition millimoles/gram of SiO ₂			
		Mg	Ti	V	Al
16	400	2.0	1.8	1.8	9
17	270	2.0	1.8	1.8	9
18	360	2.0	1.0	1.0	6
19	400	2.0	0.6	0.6	6
20	270	2.0	0.6	0.6	6
21	260	2.0	0.4	0.4	5
A*	390	2.0	0.4	0.0	5
B*	NA	NA	NA	NA	NA

* Not an example of the catalysts claimed in the present invention.

NA = Not Available

** Average particle size of the supports used is 3 microns

Table XIB
Polymer Properties

Ex. or C.E. No.	I ₂ grams per 10 min.	I ₁₀ /I ₂ Ratio	Density g/cm ³	M _w /M _n	% High Density	Cryst. onset temp. °C	z ₁ /z ₀ Ratio	Film Ultimate Stretch (percent)	Puncture (ft-lbs/in ³)
16	2.31	7.2	0.9177	3.2	24.4	111.2	0.823	330	303
17	2.33	7.2	0.9170	3.1	22.7***	111.5	0.908	340	264
18	2.38	7.1	0.9173	2.9	17.4	110.0	0.933	320	304
19*	2.24	7.3	0.9173	3.0	13.3	109.6	1.059	295	353
20*	2.37	7.3	0.9172	3.1	12.2	108.6	1.05	310	322
21*	2.39	7.5	0.9166	3.2	9.6	108.6	1.30	280**	330
A*	2.40	8.2	0.9174	3.5	11.6	----	1.18	275	291
B*	1.97	7.9	0.9208	3.9	34.0	----	----	320	225

* Not an example of films claimed in the present invention.

** Average of 2 trials (265% and 290%, rounded to nearest 5%)

*** Average of 2 trials (22.3% and 23.1%)

The following Examples 22 to 27 in Table XII summarize the catalyst formulation and product data which was observed using the process of the current invention at varying reactor temperature and targeting a 1.0 melt index, 0.920 g/cm³ density blown film product using octene as comonomer.

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Table Xi:

Ex. No.	Surface Area (m ² /gm)	Catalyst Composition millimoles/gram of SiO ₂				Polym. Temp. °C	I ₂ grams per 10 min.	I ₁₀ /I ₂ Ratio	Density g/cm ³	z ₁ /z ₀ Ratio
		Mg	Ti	V	Al					
22	374	2.0	1.8	1.8	6.5	180	0.96	7.2	0.9201	0.834
23	374	2.0	1.8	1.8	6.5	210	1.04	7.1	0.9195	0.864
24	374	2.0	1.8	1.8	6.5	225	0.97	8.0	0.9206	0.821
25	420	2.0	0.6	0.6	6.5	180	0.97	7.0	0.9201	1.11
26	420	2.0	0.6	0.6	6.5	210	1.07	7.7	0.9189	1.190
27	428	2.0	1.2	1.2	4.7	195	1.07	7.4	0.9189	0.980

EXAMPLES 28-32

These examples summarize the catalyst, formulation and product data observed using the process of the current invention at 175°C reactor temperature and targeting a 0.8 melt index, 0.905 g/cm³ density blown film product using octene as comonomer. The catalyst composition and results are given in Table XIII. The copolymers produced from the catalysts described in Table XIII clearly show an increase in z-ratio as the Mg:Ti ratio of the catalysts increases.

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Table XIII

Ex. No.	Catalyst Composition millimoles/gram of SiO ₂				Polym. Temp. °C	I ₂ grams per 10 min.	I ₁₀ /I ₂ Ratio	Density g/cm ³	z ₁ /z ₀ Ratio
	Mg	Ti	V	Al					
28	2.0	0.6	0.6	6.1	175	0.80	7.8	0.9041	1.123
29	2.0	0.2	.2	5.2	175	0.88	8.6	0.9049	1.257
30	2.0	0.2	0.2	4.5	175	0.78	8.9	0.9055	1.168
31	2.0	0.6	0.6	5.4	175	0.80	8.1	0.9058	1.109
32	2.0	0.4	0.4	4.7	175	0.80	8.2	0.9059	1.121

EXAMPLE 33

Compression molded plaques of the polymers of Examples 16 and 27 were subjected to morphological analysis at a magnification of 200X as described previously. The optical micrograph of these thin plaques indicate the spherulite size shown in Table XIII.

Comparative Example C*

For comparative purposes, a polymer was prepared using the catalyst disclosed in Example 7 of U.S. Patent 4,547,475, the disclosure of which was incorporated herein by reference.

A compression molded plaque of about 1-4 mils thickness of the polymers prepared from this catalyst was subjected to morphological analysis at a magnification of 200X. The optical micrograph of this plaque indicates the spherulite size shown in Table XIV.

Table XIV

Catalyst from	Spherulite size** (microns)
Ex. 16	10
Ex. 27	10
Comp. Ex. C*	48

**Determined by SALLS
(small angle laser light scattering)

The smaller spherulite size produced by the polymers prepared by the process of the present invention was advantageous because small spherulites typically result in improved clarity and toughness over polymers of identical structure, but having larger spherulite size.

The claims defining the invention are as follows:

1. A process for varying the short chain branching distribution (SCBD) of ethylene/ α -olefin copolymers characterized by (I) subjecting ethylene and one or more α -olefin comonomers to solution polymerization conditions in the presence of a catalyst
 5 composition comprising (A) a supported transition metal containing catalyst component comprising the product resulting from contacting (1) a porous solid inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than about 5 millimoles of hydroxyl groups per gram of support material and a particle size less than 10 microns and
 10 a surface area of from about 50 to about 800m²/g; (2) an organomagnesium compound hydrocarbon soluble organomagnesium alkoxide or hydrocarbon soluble magnesium dialkoxide; (3) a titanium compound; optionally (4) a vanadium compound; and (5) a Group IIIA metal alkyl halide; and wherein the components are employed in amounts which provide the following atomic ratios:

15 Si + Al:Mg of from about 1:1 to about 40:1;

Mg:Ti of from about 0.2:1 to about 20:1;

Mg:V of from about 0.2:1 to about 20:1 when V is present;

Mg:IIIA metal of from about 0.05:1 to about 10:1;

V:Ti of from about 0.8:1 to about 1.2:1 when V is present; and

20 (B) a co catalyst or activator for component (A); and

(II) controlling the SCBD by varying the ratio of Mg:Ti in component (A).

2. A process of claim 1 wherein

(a) said solid support material contains not greater than about 4 millimoles of hydroxyl groups per gram of support material, a particle size of from about 1 to about 8
 25 microns and a surface area of from about 150 to about 600m²/g;

(b) said transition metal catalyst contains an atomic ratio of Si + Al (from the inorganic oxide support): Mg of from about 2:1 to about 30:1;

(c) said transition metal catalyst contains an atomic ratio of Mg:Ti of from about 0.2:1 to about 10:1;

30 (d) said transition metal catalyst contains an atomic ratio of Mg:V, when present, of from about 0.2:1 to about 10:1;

(e) said transition metal catalyst contains an atomic ratio of Mg:IIIA metal of from about 0.05:1 to about 5:1; and

(f) said transition metal catalyst contains an atomic ratio of V:Ti of about 1:1.



3. A process of Claim 1 wherein

(a) said solid support material contains not greater than about 3 millimoles of hydroxyl groups per gram of support material, a particle size of from about 2 to about 5
5 microns and a surface area of from about 300 to about 500 m²/g;

(b) said transition metal catalyst contains an atomic ratio of Si + Al (from the inorganic oxide support):Mg of from about 4:1 to about 20:1;

(c) said transition metal catalyst contains an atomic ratio of Mg:Ti of from about 0.5:1 to about 10:1;

10 (d) said transition metal catalyst contains an atomic ratio of Mg:V, when present, of from about 0.5:1 to about 10:1;

(e) said transition metal catalyst contains an atomic ratio of Mg:IIIA metal of from about 0.1:1 to about 5:1; and

(f) said transition metal catalyst contains an atomic ratio of V:Ti of about 1:1.

15

4. A process of Claim 1, 2 or 3 wherein

(a) said solid support material is silica;

(b) said magnesium compound is a compound represented by the formula
20 $R_xMg(OR)_y$, wherein each R is independently a hydrocarbyl group having from 1 to about 20 carbon atoms, $x + y = 2$, and $0.5 \leq y \leq 2$;

(c) said titanium compound is a compound represented by the formula $TiX_4 - a(OR')_a$ wherein each R' is independently an alkyl group having from 1 to about 20 carbon atoms, X is a halogen atom, and a has a value from zero to 4;

25 (d) said vanadium compound, when present, is a compound represented by the formula $VX_{4-a}(OR)_a$ wherein each R' is independently an alkyl group having from 1 to about 20 carbon atoms, X is a halogen atom, and a has a value from zero to 4;

(e) said Group IIIA metal alkyl halide is a compound represented by the formula R'_yMX_z wherein M is a metal from Group IIIA of the Periodic Table of the Elements, each R' is
30 independently an alkyl group having from 1 to about 20 carbon atoms; X is a halogen atom, y and z each independently have a value from 1 to a value equal to the valence of M minus 1 and $y + z$ has a value equal to the valence of M; and

(f) said α -olefin contains from 2 to about 8 carbon atoms or any combination of any two or more of such α -olefins.

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5. A process of Claim 1, 2 or 3 wherein

(a) component (2) said magnesium compound is ethylmagnesium ethoxide, butylmagnesium ethoxide, octylmagnesium ethoxide, butylmagnesium butoxide, ethylmagnesium butoxide, butylmagnesium octoxide, s-butylmagnesium octoxide or any
5 combination of such compounds;

(b) said titanium compound is titanium tetrachloride, titanium tetraisopropoxide, or any combination of such compounds;

(c) said vanadium compound, when present is vanadium tetrachloride, vanadium oxytrichloride, or any combination of such compounds; and

10 (d) said Group IIIA metal alkyl halide is ethylaluminum dichloride, i-butylaluminum dichloride, ethylaluminum sesquichloride or any combination of such compounds; and

(e) said α -olefin is ethylene, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1 or any combination of any two or more of such compounds.

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6. The polymer prepared by the process of Claim 1, 2 or 3.

7. The polymer prepared by the process of Claim 4.

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8. The polymer prepared by the process of Claim 5.

9. The polymer resulting from polymerizing one or more α -olefins and optionally one or more polymerizable ethylenically unsaturated compounds other than an α -olefin by a process CHARACTERIZED BY contacting the materials to be polymerized with (A) a supported
25 transition metal containing catalyst component comprising the product resulting from contacting (1) a solid, porous inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina, said support material containing not greater than about 5 millimoles of hydroxyl groups per gram of support material and a particle size not greater than 10 microns and a surface area of from about 50 to
30 about 800 m²/g; (2) a hydrocarbon soluble organomagnesium alkoxide or hydrocarbon soluble magnesium dialkoxide represented by the formula R_xMg(OR)_y wherein each R is independently a hydrocarbyl group having from 1 to about 20 carbon atoms; x + y = 2; and 0.5 ≤ y ≤ 2; (3) a titanium compound; optionally (4) a vanadium compound; and (5) a Group IIIA metal alkyl halide; and wherein the components are employed in amounts which provide the following
35 atomic ratios:

Si + Al (from the inorganic oxide support): Mg of from about 1:1 to about 70:1;

Mg:Ti of from about 0.1:1 to about 40:1;

Mg:V, when present, of from about 0.1:1 to about 40:1;

Mg:III A metal of from about 0.01:1 to about 100:1;

V:Ti of from about 0:1 to about 10:1; and

(B) a cocatalyst or activator for component (A).

5 10. The polymer of Claim 9 wherein

(a) said solid support material contains not greater than about 4 millimoles of hydroxyl groups per gram of support material, a particle size of from about 1 to about 8 microns and a surface area of from about 150 to about 600 m²/g;

(b) said transition metal catalyst contains an atomic ratio of Si + Al (from the inorganic oxide support):Mg of from about 2:1 to about 40:1;

(c) said transition metal catalyst contains an atomic ratio of Mg:Ti of from about 0.2:1 to about 20:1;

(d) said transition metal catalyst contains an atomic ratio of Mg:V, when present, of from about 0.2:1 to about 20:1;

15 (e) said transition metal catalyst contains an atomic ratio of Mg:III A metal of from about 0.05:1 to about 10:1; and

(f) said transition metal catalyst contains an atomic ratio of V:Ti of from about 0:1 to about 5:1.

11. The polymer of Claim 9 wherein

20 (a) said solid support material contains not greater than about 3 millimoles of hydroxyl groups per gram of support material, a particle size of from about 2 to about 5 microns and a surface area of from about 300 to about 500 m²/g;

(b) said transition metal catalyst contains an atomic ratio of Si + Al (from the inorganic oxide support):Mg of from about 4:1 to about 20:1;

25 (c) said transition metal catalyst contains an atomic ratio of Mg:Ti of from about 0.5:1 to about 10:1;

(d) said transition metal catalyst contains an atomic ratio of Mg:V, when present, of from about 0.5:1 to about 10:1;

30 (e) said transition metal catalyst contains an atomic ratio of Mg:III A metal of from about 0.1:1 to about 5:1; and

(f) said transition metal catalyst contains an atomic ratio of V:Ti of from about 0:1 to about 1:1.

12. The polymer of Claim 9, 10 or 11 wherein

35 (a) said solid support material is silica,

(b) said titanium compound is a compound represented by the formula TiX₄._a(OR')_a wherein each R' is independently an alkyl group having from 1 to about 20 carbon atoms, X is a halogen atom, and a has a value from zero to 4;

(c) said vanadium compound, when present, is a compound represented by the formula $VX_{4-a}(OR)_a$ wherein each R is independently an alkyl group having from 1 to about 20 carbon atoms, X is a halogen atom, and has a value from zero to 4;

(d) said Group IIIA metal alkyl halide is a compound represented by the formula R'_yMX_z wherein M is a metal from Group IIIA of the Periodic Table of the Elements, each R' is independently an alkyl group having from 1 to about 20 carbon atoms; X is a halogen atom, y and z each independently have a value from 1 to a value equal to the valence of M minus 1 and $y + z$ has a value equal to the valence of M; and

(e) said α -olefin contains from 2 to about 8 carbon atoms or any combination of any two or more of such α -olefins.

13. The polymer of claim 9, 10 or 11 wherein

(a) component (2) is ethylmagnesium ethoxide, butylmagnesium ethoxide, octylmagnesium ethoxide, butylmagnesium butoxide, ethylmagnesium butoxide, butylmagnesium octoxide, s-butylmagnesium octoxide or any combination of such compounds;

(b) said titanium compound is titanium tetrachloride, titanium tetraisopropoxide, or any combination of such compounds;

(c) said vanadium compound, when present, is vanadium tetrachloride, vanadium oxytrichloride, or any combination of such compounds; and

(d) said Group IIIA metal alkyl halide is ethylaluminum dichloride, 1-butylaluminum dichloride, ethylaluminum sesquichloride or any combination of such compounds; and

(e) said α -olefin is ethylene, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1 or any combination of any two or more of such compounds.

14. The polymer of claim 9, 10 or 11, wherein the polymer is characterized as having greater than about 17 percent high density fraction and a M_w/M_n ratio of less than about 3.6.

15. The polymer of claim 9, 10 or 11, wherein the polymer is characterized as having greater than 20 percent high density fraction and a M_w/M_n ratio of less than about 3.3.

16. A polymer resulting from polymerizing one or more α -olefins and optionally one or more polymerizable ethylenically unsaturated compounds other than an α -olefin, substantially as hereinbefore described with reference to any one of the Examples.

17. A film comprising the polymer of any one of claims 9-16.

18. The film of claim 17, wherein the film is a cast film having a gauge of from about 0.4 to about 1.2 mils (about 10 to about 30 μ m), a percent ultimate stretchability of at least about 295 percent and a puncture of at least about 250ft-lbs/cm³ (about 339J/cm³).

19. The film of claim 18, wherein the polymer has a density of from about 0.905g/cm³ to about 0.935g/cm³ and a melt index of from about 0.6g/10 minutes to about 6g/10 minutes.



20. The film of claim 19, wherein the polymer is an ethylene/1-octene copolymer.

21. The film of claim 20, wherein the film gauge is about 0.8mils (about 20 μ m) and the percent ultimate stretchability is at least about 320 percent.

22. A film comprising the polymer of claim 14 or 15, wherein the film is
5 characterized as having a gauge of from about 0.4 to about 1.2mils (about 10 to about 30 μ m) a percent ultimate stretchability of at least about 380 percent, and a puncture resistance of at least about 250ft-lbs/cm³ (about 339J/cm³).

23. The film of claim 18, wherein the polymer is further characterized as having a
10 density of from about 0.905g/cm³ to about 0.935g/cm³ and a melt index of from about 0.6g/10 minutes to about 6g/10 minutes.

24. A process for varying the short chain branching distribution (SCBD) of ethylene/ α -olefin copolymers, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

Dated 11 February, 1997
The Dow Chemical Company

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON



INTERNATIONAL SEARCH REPORT

PCT/US 93/02751

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5	C08F10/00;	C08F4/655; C08L23/16; C08J5/18
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F ; C08L ; C08J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P, X	WO, A, 9 213 009 (THE DOW CHEMICAL COMPANY) 6 August 1992 see the whole document ---	9-13
A	EP, A, 0 435 627 (MOBIL OIL CORPORATION) 3 July 1991 see abstract; claims 1, 4, 9 see page 2, line 1 - line 6 see page 3, line 53 - page 4, line 3 ---	1
A	GB, A, 2 189 252 (CHEMOPETROL KONCERNOVA UCELOVA ORGANIZACE) 21 October 1987 see claims 1-3; table 1 ---	
A	US, A, 4 558 024 (STEVEN A. BEST) 10 December 1985 see example 3 ---	
-/--		
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Commencement of the International Search	Date of Mailing of this International Search Report	
08 SEPTEMBER 1993	1 2. 10. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	FISCHER B.R.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 324 588 (MOBIL OIL CORPORATION) 19 July 1989 see example 1	
A	US,A,4 243 619 (FRASER W. A.) 6 January 1981 see example 17 JOURNAL OF PLASTIC FILM & SHEETING vol. 4, July 1988, DOHRER K.K. 'Short Chain Branching Distribution of ULDPE' cited in the application see the whole document	14-24
A	EP,A,0 100 689 (SOCIETE CHIMIQUE DES CHARBONNAGES) 15 February 1984 see claims 1,3,5,10 see page 1, line 32 - page 2, line 4	14-24

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 93/02751

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1: Claims 1-13, 1-8, 9-13

2: Claims 14-24

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

 The additional search fees were accompanied by the applicant's protest. No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9302751
SA 72012

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 08/09/93

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		JP-B- 3073582	22-11-91
		JP-A- 58210948	08-12-83

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/81