EXHIBIT V

PART 6

US005272236A

United States Patent [19]

Lai et al.

[11] Patent Number: 5,272,236

[45] Date of Patent: Dec. 21, 1993

[54] **ELASTIC SUBSTANTIALLY LINEAR OLEFIN POLYMERS**

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[21] Appl. No.: **776,130**

[22] Filed: **Oct. 15, 1991**

[51] **Int. Cl.**[5] **C08F 210/08; C08F 210/14**

[52] **U.S. Cl.** **526/348.5**; 526/127; 526/160; 526/170; 526/348.2; 526/348.4; 526/348.6; 502/152

[58] **Field of Search** 526/160, 170, 127, 348, 526/348.2, 348.4, 348.5, 348.6

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Attorney, Agent, or Firm—Stephen P. Krupp; L. Wayne White

[57] **ABSTRACT**

Substantially linear olefin polymers having a melt flow ratio, I_{10}/I_2, ≥ 5.63, a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leq (I_{10}/I_2)-4.63$, and a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2 and their method of manufacture are disclosed. The substantially linear olefin polymers preferably have at least about 0.01 long chain branches/1000 carbons and a molecular weight distribution from about 1.5 to about 2.5. The new polymers have improved processability over conventional olefin polymers and are useful in producing fabricated articles such as fibers, films, and molded parts.

38 Claims, 5 Drawing Sheets

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FIG. 1

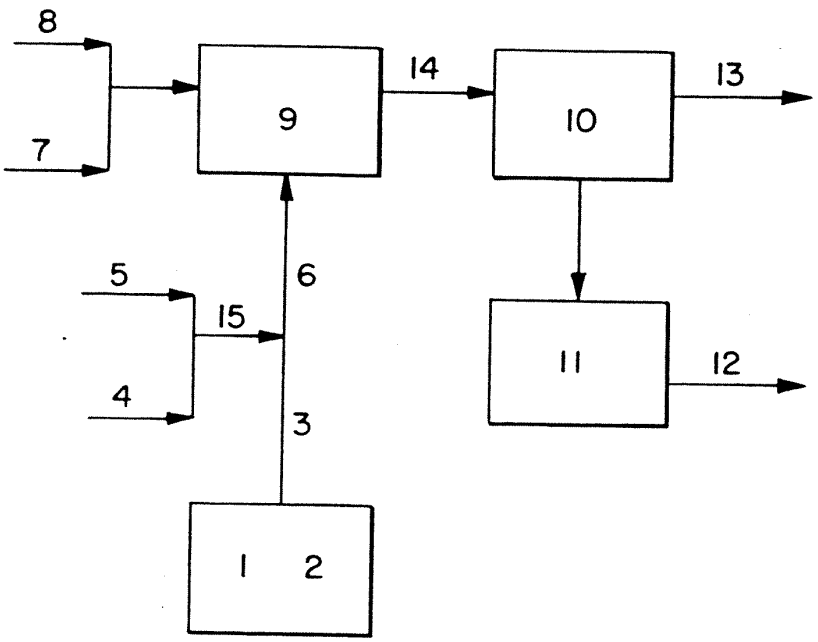


FIG. 2

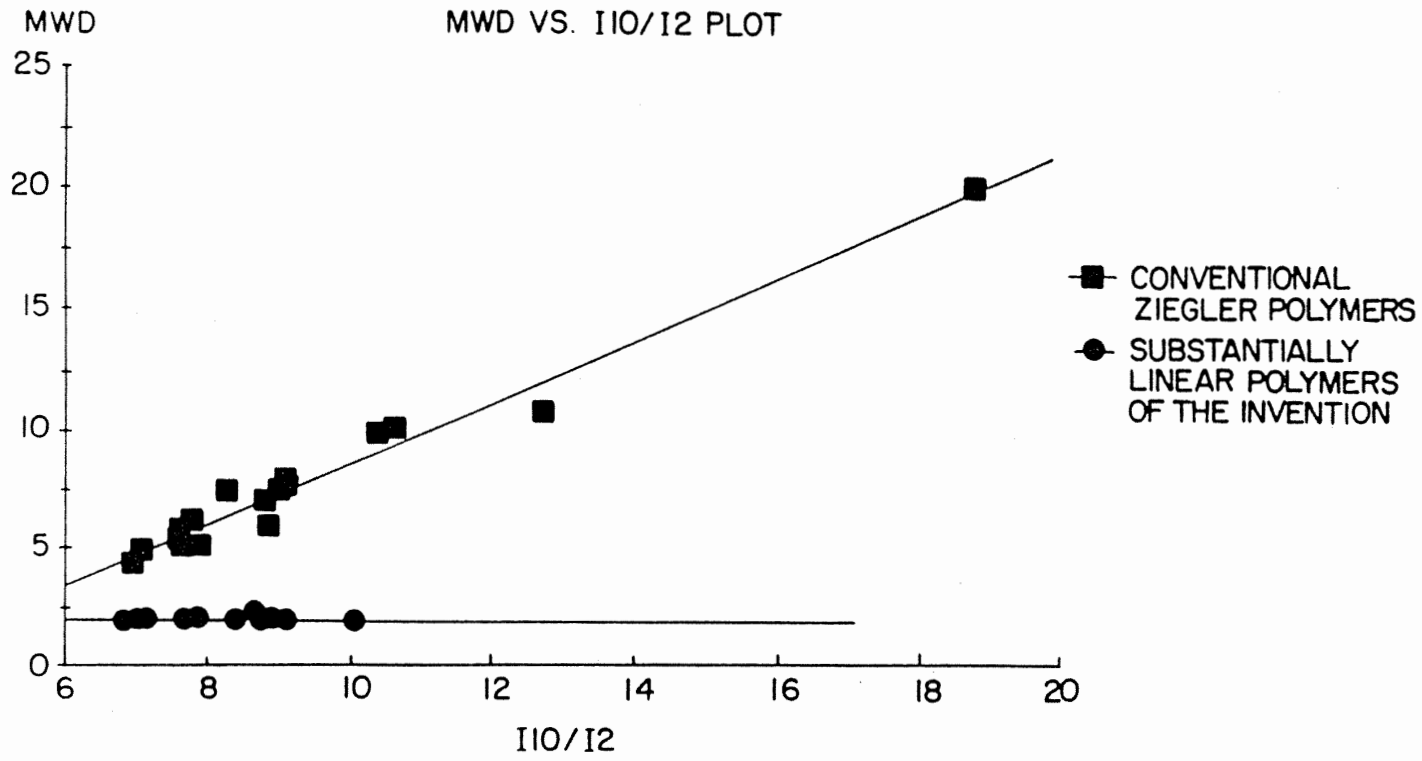

MWD
MWD VS. I10/I2 PLOT
25
20
15
10
5
0
6
8
10
12
14
16
18
20
I10/I2
CONVENTIONAL ZIEGLER POLYMERS
SUBSTANTIALLY LINEAR POLYMERS OF THE INVENTION

FIG. 3

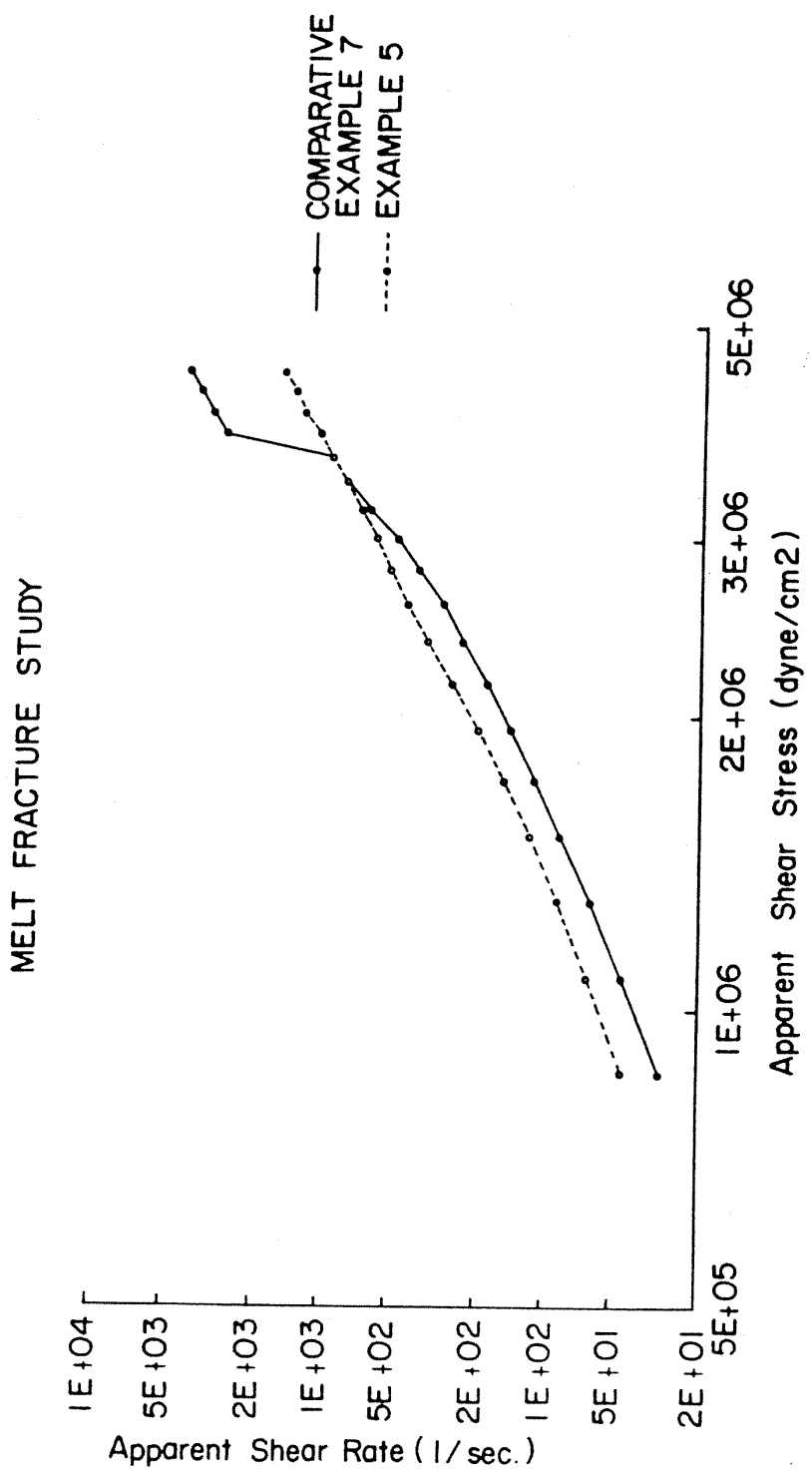

MELT FRACTURE STUDY
COMPARATIVE EXAMPLE 7
EXAMPLE 5
1E+04
5E+03
2E+03
1E+03
5E+02
2E+02
1E+02
5E+01
2E+01
Apparent Shear Rate (1/sec.)
5E+05
1E+06
2E+06
3E+06
5E+06
Apparent Shear Stress (dyne/cm2)

FIG. 4

MELT FRACTURE STUDY

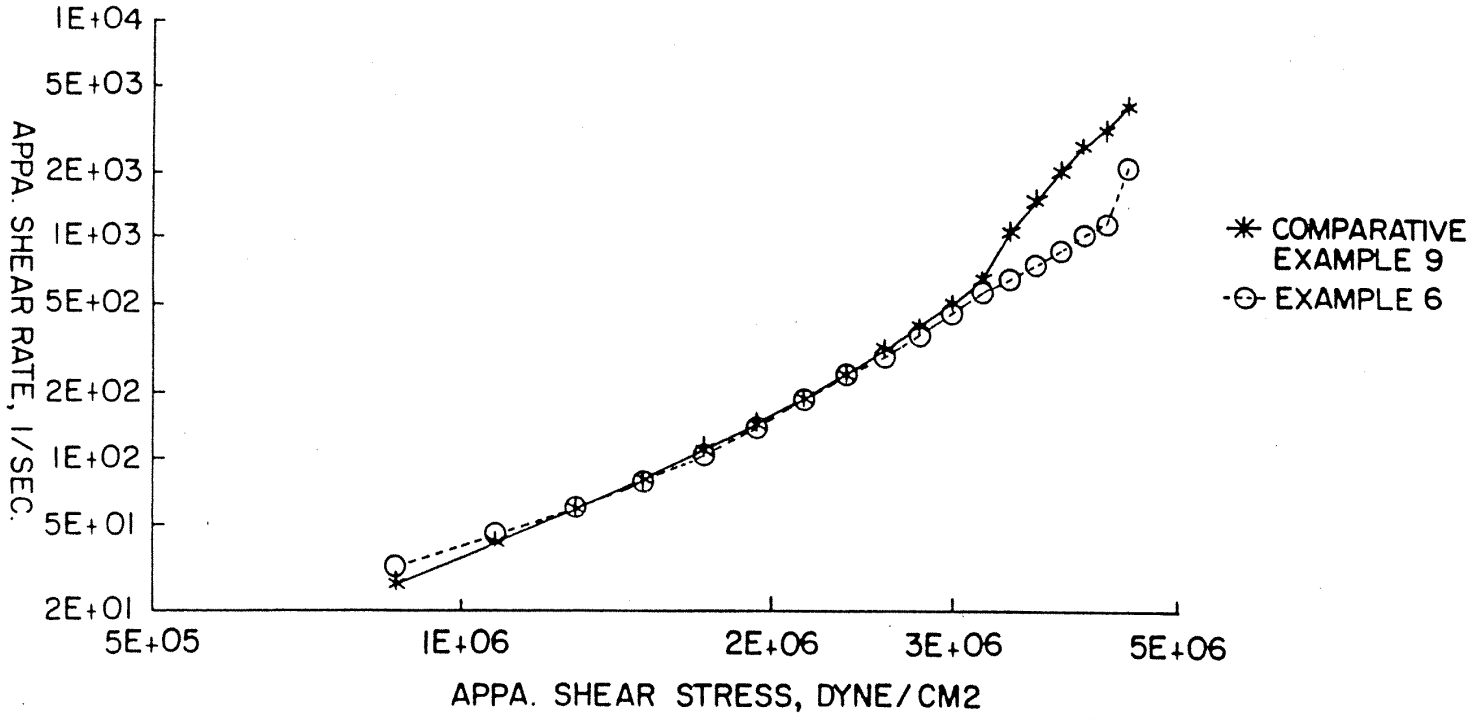
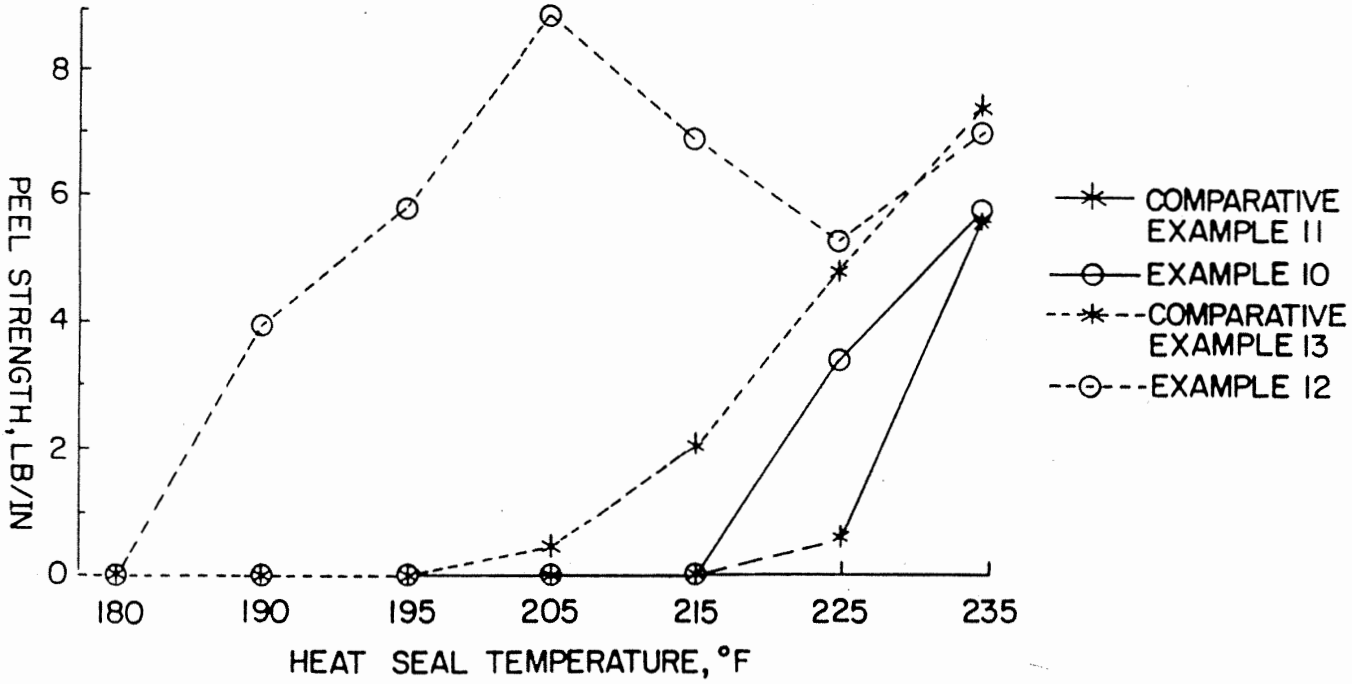


FIG. 5

HEAT SEAL PERFORMANCE COMPARISON



ELASTIC SUBSTANTIALLY LINEAR OLEFIN POLYMERS

FIELD OF THE INVENTION

This invention relates to elastic substantially linear olefin polymers having improved processability, e.g., low susceptibility to melt fracture, even under high shear stress extrusion conditions. Methods of manufacturing these polymers are also disclosed.

BACKGROUND OF THE INVENTION

Molecular weight distribution (MWD), or polydispersity, is a well known variable in polymers. The molecular weight distribution, sometimes described as the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) (i.e., M_w/M_n) can be measured directly, e.g., by gel permeation chromatography techniques, or more routinely, by measuring I_{10}/I_2 ratio, as described in ASTM D-1238. For linear polyolefins, especially linear polyethylene, it is well known that as M_w/M_n increases, I_{10}/I_2 also increases.

John Dealy in "Melt Rheology and Its Role in Plastics Processing" (Van Nostrand Reinhold, 1990) page 597 discloses that ASTM D-1238 is employed with different loads in order to obtain an estimate of the shear rate dependence of melt viscosity, which is sensitive to weight average molecular weight (M_w) and number average molecular weight (M_n).

Bersted in *Journal of Applied Polymer Science* Vol. 19, page 2167–2177 (1975) theorized the relationship between molecular weight distribution and steady shear melt viscosity for linear polymer systems. He also showed that the broader MWD material exhibits a higher shear rate or shear stress dependency.

Ramamurthy in *Journal of Rheology*, 30(2), 337–357 (1986), and Moynihan, Baird And Ramanathan in *Journal of Non-Newtonian Fluid Mechanics*, 36, 255–263 (1990), both disclose that the onset of sharkskin (i.e., melt fracture) for linear low density polyethylene (LLDPE) occurs at an apparent shear stress of $1–1.4 \times 10^6$ dyne/cm^2, which was observed to be coincident with the change in slope of the flow curve. Ramamurthy also discloses that the onset of surface melt fracture or of gross melt fracture for high pressure low density polyethylene (HP-LDPE) occurs at an apparent shear stress of about 0.13 MPa (1.3×10^6 dynes/cm^2).

Kalika and Denn in *Journal of Rheology*, 31, 815–834 (1987) confirmed the surface defects or sharkskin phenomena for LLDPE, but the results of their work determined a critical shear stress of 2.3×10^6 dyne/cm^2, significantly higher than that found by Ramamurthy and Moynihan et al.

International Patent Application (Publication No. WO 90/03414) published Apr. 5, 1990, discloses linear ethylene interpolymer blends with narrow molecular weight distribution and narrow short chain branching distributions (SCBDS). The melt processibility of the interpolymer blends is controlled by blending different molecular weight interpolymers having different narrow molecular weight distributions and different SCBDs.

Exxon Chemical Company, in the Preprints of Polyolefins VII International Conference, page 45–66, Feb. 24–27 1991, disclose that the narrow molecular weight distribution (NMWD) resins produced by their EXXPOL TM technology have higher melt viscosity and lower melt strength than conventional Ziegler resins at the same melt index. In a recent publication, Exxon Chemical Company has also taught that NMWD polymers made using a single site catalyst create the potential for melt fracture ("New Specialty Linear Polymers (SLP) For Power Cables," by Monica Hendewerk and Lawrence Spenadel, presented at IEEE meeting in Dallas, Tex., September, 1991).

Previously known narrow molecular weight distribution linear polymers disadvantageously possessed low shear sensitivity or low I_{10}/I_2 value, which limits the extrudability of such polymers. Additionally, such polymers possessed low melt elasticity, causing problems in melt fabrication such as film forming processes or blow molding processes (e.g., sustaining a bubble in the blown film process, or sag in the blow molding process etc.). Finally, such resins also experienced melt fracture surface properties at relatively low extrusion rates thereby processing unacceptably.

SUMMARY OF THE INVENTION

We have now discovered a new family of substantially linear olefin polymers which have many improved properties and a method of their manufacture. The substantially linear olefin polymers have (1) high melt elasticity and, (2) relatively narrow molecular weight distributions with exceptionally good processibility while maintaining good mechanical properties and (3) they do not melt fracture over a broad range of shear stress conditions. These properties are obtained without benefit of specific processing additives. The new polymers can be successfully prepared in a continuous polymerization process using constrained geometry catalyst technology, especially when polymerized utilizing solution process technology.

The improved properties of the polymers include improved melt elasticity and processability in thermal forming processes such as extrusion, blowing film, injection molding and blowmolding.

Substantially linear polymers made according to the present invention have the following novel properties:

a) a melt flow ratio, I_{10}/I_2, $\geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a polymerization process suitable for making the polymers of the present invention.

FIG. 2 plots data describing the relationship between I_{10}/I_2 and M_w/M_n for polymer Examples 5 and 6 of the invention, and from comparative examples 7–9.

FIG. 3 plots the shear stress versus shear rate for Example 5 and comparative example 7, described herein.

FIG. 4 plots the shear stress versus shear rate for Example 6 and comparative example 9, described herein.

FIG. 5 plots the heat seal strength versus heat seal temperature of film made from Examples 10 and 12, and comparative examples 11 and 13, described herein.

DETAILED DESCRIPTION OF THE INVENTION

Other properties of the substantially linear polymers include:

a) a density from about 0.85 grams/cubic centimeter (g/cc) to about 0.97 g/cc (tested in accordance with ASTM D-792), and

b) a melt index, MI, from about 0.01 grams/10 minutes to about 1000 gram/10 minutes.

Preferably the melt flow ratio, I_{10}/I_2, is from about 7 to about 20.

The molecular weight distribution (i.e., M_w/M_n) is preferably less than about 5, especially less than about 3.5, and most preferably from about 1.5 to about 2.5.

Throughout this disclosure, "melt index" or "I_2" is measured in accordance with ASTM D-1238 (190/2.16); "I_{10}" is measured in accordance with ASTM D-1238 (190/10).

The melt tension of these new polymers is also surprisingly good, e.g., as high as about 2 grams or more, especially for polymers which have a very narrow molecular weight distribution (i.e., M_w/M_n from about 1.5 to about 2.5).

The substantially linear polymers of the present invention can be homopolymers of C_2–C_{20} olefins, such as ethylene, propylene, 4-methyl-1-pentene, etc., or they can be interpolymers of ethylene with at least one C_3–C_{20} α-olefin and/or C_2–C_{20} acetylenically unsaturated monomer and/or C_4–C_{18} diolefins. The substantially linear polymers of the present invention can also be interpolymers of ethylene with at least one of the above C_3–C_{20} α-olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers.

Monomers usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, polyenes, carbon monoxide, etc. Preferred monomers include the C_{2-10} α-olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (e.g., cyclo-pentene, cyclo-hexene and cyclo-octene).

The term "substantially linear" polymers means that the polymer backbone is either unsubstituted or substituted with up to 3 long chain branches/1000 carbons. Preferred polymers are substituted with about 0.01 long chain branches/1000 carbons to about 3 long chain branches/1000 carbons, more preferably from about 0.01 long chain branches/1000 carbons to about 1 long chain branches/1000 carbons, and especially from about 0.3 long chain branches/1000 carbons to about 1 long chain branches/1000 carbons.

Long chain branching is defined herein as a chain length of at least about 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy. The long chain branch can be as long as about the same length as the length of the polymer back-bone.

Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method of Randall (*Rev. Macromol. Chem. Phys.*, C29 (2&3), p. 285–297), the disclosure of which is incorporated herein by reference.

"Melt tension" is measured by a specially designed pulley transducer in conjunction with the melt indexer. Melt tension is the load that the extrudate or filament exerts while passing over the pulley at the standard speed of 30 rpm. The melt tension measurement is similar to the "Melt Tension Tester" made by Toyoseiki and is described by John Dealy in "Rheometers for Molten Plastics", published by Van Nostrand Reinhold Co. (1982) on page 250–251.

The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R. N. Shroff and L. V. Cancio in *Polymer Engineering Science*, Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97, both publications of which are incorporated by reference herein in their entirety. All GER experiments are performed at a temperature of 190° C., at nitrogen pressures between 5250 to 500 psig using a 0.0296 inch diameter, 20:1 L/D die. An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in *Journal of Rheology*, 30(2), 337–357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. Preferably, the critical shear stress at the OGMF and the critical shear stress at the OSMF for the substantially linear ethylene polymers described herein is greater than about 4×10^6 dyne/cm^2 and greater than about 2.8×10^6 dyne/cm^2, respectively.

For the polymers described herein, the PI is the apparent viscosity (in Kpoise) of a material measured by GER at a temperature of 190° C., at nitrogen pressure of 2500 psig using a 0.0296 inch diameter, 20:1 L/D die, or corresponding apparent shear stress of 2.15×10^6 dyne/cm^2. The novel polymers described herein preferably have a PI in the range of about 0.01 kpoise to about 50 kpoise, preferably about 15 kpoise or less.

The SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of an polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, *Journal of Polymer Science, Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), or in U.S. Pat. No. 4,798,081, both disclosures of which are incorporated herein by reference. The SCBDI or CDBI for the new polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent.

The most unique characteristic of the presently claimed polymers is a highly unexpected flow property as shown in FIG. 2, where the I_{10}/I_2 value is essentially independent of polydispersity index (i.e. M_w/M_n). This is contrasted with conventional polyethylene resins having rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases. Measurement of the polydispersity index is done according to the following technique:

The polymers are analyzed by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three linear mixed bed columns (Polymer Laboratories (10 micron particle size)), operating at a system temperature of 140° C. The solvent is 1,2,4-trichlorobenzene, from which about 0.5% by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliter/minute and the injection size is 100 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are 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:

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

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

$$M_w = (R)(w_i)(M_i)$$

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

Another highly unexpected characteristic of the polymers of the present invention is their non-susceptibility to melt fracture or the formation of extrudate defects during high pressure, high speed extrusion. Preferably, polymers of the present invention do not experience "sharkskin" or surface melt fracture during the GER extrusion process even at an extrusion pressure of 5000 psi and corresponding apparent stress of 4.3×10^6 dyne/cm^2. In contrast, a conventional LLDPE experiences "sharkskin" or onset of surface melt fracture (OSMF) at an apparent stress under comparable conditions as low as $1.0–1.4 \times 10^6$ dyne/cm^2.

Improvements of melt elasticity and processibility over conventional LLDPE resins with similar MI are most pronounced when I_2 is lower than about 3 grams/10 minutes. Improvements of physical properties such as strength properties, heat seal properties, and optical properties, over the conventional LLDPE resins with similar MI, are most pronounced when I_2 is lower than about 100 grams/10 minutes. The substantially linear polymers of the present invention have processibility similar to that of High Pressure LDPE while possessing strength and other physical properties similar to those of conventional LLDPE, without the benefit of special adhesion promoters (e.g., processing additives such as Viton TM fluoroelastomers made by E. I. DuPont de Nemours & Company).

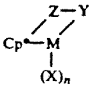
The improved melt elasticity and processibility of the substantially linear polymers according to the present invention result, it is believed, from their method of production. The polymers may be produced via a continuous controlled polymerization process using at least one reactor, but can also be produced using multiple reactors (e.g., using a multiple reactor configuration as described in U.S. Pat. No. 3,914,342, incorporated herein by reference) at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties. According to one embodiment of the present process, the polymers are produced in a continuous process, as opposed to a batch process. Preferably, the polymerization temperature is from about 20° C. to about 250° C., using constrained geometry catalyst technology. If a narrow molecular weight distribution polymer (M_w/M_n of from about 1.5 to about 2.5) having a higher I_{10}/I_2 ratio (e.g. I_{10}/I_2 of about 7 or more, preferably at least about 8, especially at least about 9) is desired, the ethylene concentration in the reactor is preferably not more than about 8 percent by weight of the reactor contents, especially not more than about 4 percent by weight of the reactor contents. Preferably, the polymerization is performed in a solution polymerization process. Generally, manipulation of I_{10}/I_2 while holding M_w/M_n relatively low for producing the novel polymers described herein is a function of reactor temperature and/or ethylene concentration. Reduced ethylene concentration and higher temperature generally produces higher I_{10}/I_2.

Suitable catalysts for use herein preferably include constrained geometry catalysts as disclosed in U.S. application Ser. Nos.: 545,403, filed Jul. 3, 1990; 758,654, filed Sep. 12, 1991; 758,660, filed Sep. 12, 1991; and 720,041, filed Jun. 24, 1991, the teachings of all of which are incorporated herein by reference.

The monocyclopentadienyl transition metal olefin polymerization catalysts taught in U.S. Pat. No. 5,026,798, the teachings of which are incorporated herein by reference, are also suitable for use in preparing the polymers of the present invention.

The foregoing catalysts may be further described as comprising a metal coordination complex comprising a metal of groups 3–10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized π-bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted π-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π-bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π-bonded moiety. The catalyst further comprises an activating cocatalyst.

Preferred catalyst complexes correspond to the formula:



(I)

wherein:

M is a metal of group 3–10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

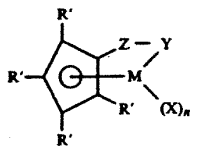
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

Y is an anionic or nonanionic ligand group bonded to Z and 51 comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system.

More preferably still, such complexes correspond to the formula:



wherein R' each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms;

X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, neutral Lewis base ligands and combinations thereof having up to 20 non-hydrogen atoms;

Y is —O—, —S—, —NR*—, —PR*—, or a neutral two electron donor ligand selected from the group consisting of OR*, SR*, NR*$_2$, or PR*$_2$;

M is a previously defined; and

Z is SiR*$_2$, CR*$_2$, SiR*$_2$SiR*$_2$, CR*$_2$CR*$_2$, CR*=CR*, CR*$_2$SiR*$_2$, GeR*$_2$, BR*, BR*$_2$; wherein:

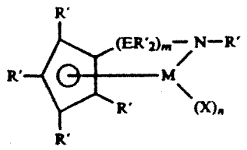
R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and

n is 1 or 2.

It should be noted that whereas formula I and the following formulas indicate a cyclic structure for the catalysts, when Y is a neutral two electron donor ligand, the bond between M and Y is more accurately referred to as a coordinate-covalent bond. Also, it should be noted that the complex may exist as a dimer or higher oligomer.

Further preferably, at least one of R', Z, or R* is an electron donating moiety. Thus, highly preferably Y is a nitrogen or phosphorus containing group corresponding to the formula —N(R'"— or —P(R'")—, wherein R'" is C$_{1-10}$ alkyl or aryl, i.e. an amido or phosphido group.

Most highly preferred complex compounds are amidosilane- or amidoalkanediyl- compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, aryl, aryloxy or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2.

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc. Specific compounds include: (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (tert-butylamido)(tetra-methyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido) (tetramethyl-η^5-cycloperitadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido)(tetramethyl-η^5-cyclopentadienyl)-methylenetitanium dichloro, (tert-butylamido)dibenzyl(tetramethyl-η^5-cyclopentadienyl) silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dichloride, (phenylphosphido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanezirconium dibenzyl, (tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dimethyl, and the like.

The complexes may be prepared by contacting a derivative of a metal, M, and a group I metal derivative or Grignard derivative of the cyclopentadienyl compound in a solvent and separating the salt byproduct. Suitable solvents for use in preparing the metal complexes are aliphatic or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane, heptane, tetrahydrofuran, diethyl ether, benzene, toluene, xylene, ethylbenzene, etc., or mixtures thereof.

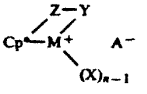
In a preferred embodiment, the metal compound is MX_{n+1}, i.e. M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. The oxidation is accomplished merely by contacting the reactants utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "noninterfering oxidizing agent" is meant a compound having an oxidation

potential sufficient to raise the metal oxidation state without interfering with the desired complex formation or subsequent polymerization processes. A particularly suitable noninterfering oxidizing agent is AgCl or an organic halide such as methylene chloride. The foregoing techniques are disclosed in U.S. Ser. Nos.: 545,403, filed Jul. 3, 1990 and 702,475, filed May 20, 1991, the teachings of both of which are incorporated herein by reference.

Additionally the complexes may be prepared according to the teachings of the copending application entitled: "Preparation of Metal Coordination Complex (I)", filed in the names of Peter Nickias and David Wilson, on Oct. 15, 1991 and the copending application entitled: "Preparation of Metal Coordination Complex (II)", filed in the names of Peter Nickias and David Devore, on Oct. 15, 1991, the teachings of which are incorporated herein by reference thereto.

Suitable cocatalysts for use herein include polymeric or oligomeric alumoxanes, especially methyl alumoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Preferred cocatalysts are inert, noncoordinating, boron compounds.

Ionic active catalyst species which can be used to polymerize the polymers described herein correspond to the formula:



wherein:

M is a metal of group 3–10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1 , 2, 3, or 4 and is 2 less than the valence of M; and

A^- is a noncoordinating, compatible anion.

One method of making the ionic catalyst species which can be utilized to make the polymers of the present invention involve combining:

a) at least one first component which is a mono(cyclopentadienyl) derivative of a metal of Group 3–10 or the Lanthanide Series of the Periodic Table of the Elements containing at least one substituent which will combine with the cation of a second component (described hereinafter) which first component is capable of forming a cation formally having a coordination number that is one less than its valence, and

b) at least one second component which is a salt of a Bronsted acid and a noncoordinating, compatible anion.

More particularly the noncoordinating, compatible anion of the Bronsted acid salt may comprise a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and non-nucleophilic. The recitation "metalloid", as used herein, includes non-metals such as boron, phosphorus and the like which exhibit semi-metallic characteristics.

Illustrative, but not limiting examples of monocyclopentadienyl metal components (first components) which may be used in the preparation of cationic complexes are derivatives of titanium, zirconium, hafnium, chromium, lanthanum, etc. Preferred components are titanium or zirconium compounds. Examples of suitable monocyclopentadienyl metal compounds are hydrocarbyl-substituted monocyclopentadienyl metal compounds such as (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dimethyl, (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dibenzyl, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (ethylamido)(tetramethyl-η^5-cyclopentadienyl)-methylenetitanium dimethyl, (tert-butylamido)dibenzyl(tetramethyl-η^5-cyclopentadienyl)silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium diphenyl, (phenylphosphido)dimethyl(tetramethyl-η^5-cyclopentadienyl)-silanezirconium dibenzyl, and the like.

Such components are readily prepared by combining the corresponding metal chloride with a dilithium salt of the substituted cyclopentadienyl group such as a cyclopentadienyl-alkanediyl, cyclopentadienyl—silane amide, or cyclopentadienyl—phosphide compound. The reaction is conducted in an inert liquid such as tetrahydrofuran, C_{5-10} alkanes, toluene, etc. utilizing conventional synthetic procedures. Additionally, the first components may be prepared by reaction of a group II derivative of the cyclopentadienyl compound in a solvent and separating the salt by-product. Magnesium derivatives of the cyclopentadienyl compounds are preferred. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. The resulting metal cyclopentadienyl halide complexes may be alkylated using a variety of techniques. Generally, the metal cyclopentadienyl alkyl or aryl complexes may be prepared by alkylation of the metal cyclopentadienyl halide complexes with alkyl or aryl derivatives of group I or group II metals. Preferred alkylating agents are alkyl lithium and Grignard derivatives using conventional synthetic techniques. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. A preferred solvent is a mixture of toluene and tetrahydrofuran.

Compounds useful as a second component in the preparation of the ionic catalysts useful in this invention will comprise a cation, which is a Bronsted acid capable of donating a proton, and a compatible noncoordinating anion. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 3–10 or Lanthanide Series cation) which is formed when the two components are combined and sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Suitable metals, then, include, but are Rot limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions

which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

Highly preferably, the second component useful in the preparation of the catalysts of this invention may be represented by the following general formula:

$$(L-H)^+[A]$$

wherein:

L is a neutral Lewis base;

$(L-H)^+$ is a Bronsted acid; and

$[A]^-$ is a compatible, noncoordinating anion.

More preferably $[A]^-$ corresponds to the formula:

$$[M'Q_q]^-$$

wherein:

M' is a metal or metalloid selected from Groups 5–15 of the Periodic Table of the Elements; and

Q independently each occurrence is selected from the Group consisting of hydride, dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide and

q is one more than the valence of M'.

Second components comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

$$[L-H]^+[BQ_4]$$

wherein:

L is a neutral Lewis base;

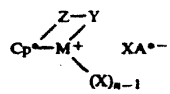
$[L-H]^+$ is a Bronsted acid;

B is boron in a valence state of 3; and

Q is as previously defined.

Illustrative, but not limiting, examples of boron compounds which may be used as a second component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, trimethylammonium tetra(p-tolylborate), tributylammonium tetrakis-pentafluorophenylborate, tripropylammonium tetrakis-2,4-dimethylphenylborate, tributylammonium tetrakis-3,5-dimethylphenylborate, triethylammonium tetrakis-(3,5-di-trifluoromethylphenyl)borate and the like. Also suitable are N,N-dialkyl anilinium salts such as N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-2,4,6-pentamethylanilinium tetraphenylborate and the like; dialkyl ammonium salts such as di-(i-propyl)ammonium tetrakispentafluorophenylborate, dicyclohexylammonium tetraphenylborate and the like; and triaryl phosphonium salts such as triphenylphosphonium tetraphenylborate, tri(methylphenyl)phosphonium tetrakis-pentafluorophenylborate, tri(dimethylphenyl)phosphonium tetraphenylborate and the like.

Preferred ionic catalysts are those having a limiting charge separated structure corresponding to the formula:



wherein:

M is a metal of group 3–10, or the Lanthanide series of the Periodic Table of the Elements;

Cp^* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

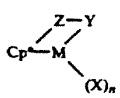
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp^* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

XA^*- is $-XB(C_6F_5)_3$.

This class of cationic complexes may be conveniently prepared by contacting a metal compound corresponding to the formula:



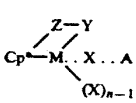
wherein:

Cp, M, and n are as previously defined,

with tris(pentafluorophenyl)borane cocatalyst under conditions to cause abstraction of X and formation of the anion $-XB(C_6F_5)_3$.

Preferably X in the foregoing ionic catalyst is C_1–C_{10} hydrocarbyl, most preferably methyl.

The preceding formula is referred to as the limiting, charge separated structure. However, it is to be understood that, particularly in solid form, the catalyst may not be fully charge separated. That is, the X group may retain a partial covalent bond to the metal atom, M. Thus, the catalysts may be alternately depicted as possessing the formula:



The catalysts are preferably prepared by contacting the derivative of a Group 4 or Lanthanide metal with the tris(pentafluorophenyl)borane in an inert diluent such as an organic liquid.

Tris(pentafluorphenyl)borane is a commonly available Lewis acid that may be readly prepared according to known techniques. The compound is disclosed in Marks, et al. *J. Am. Chem. Soc.* 1991, 113, 3623–3625 for use in alkyl abstraction of zirconocenes.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table

of the Elements using the IUPAC system for numbering groups.

It is believed that in the constrained geometry catalysts used herein the metal atom is forced to greater exposure of the active metal site because one or more substituents on the single cyclopentadienyl or substituted cyclopentadienyl group forms a portion of a ring structure including the metal atom, wherein the metal is both bonded to an adjacent covalent moiety and held in association with the cyclopentadienyl group through an η^5 or other η-bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is, the metal may be symmetrically or unsymmetrically π-bound to the cyclopentadienyl or substituted cyclopentadienyl group.

The geometry of the active metal site is further defined as follows. The centroid of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The angle, Θ, formed at the metal center between the centroid of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, Θ, is less than in a similar, comparative complex differing only in the fact that the constrain-inducing substituent is replaced by hydrogen have constrained geometry for purposes of the present invention. Preferably one or more of the above angles, Θ, decrease by at least 5 percent, more preferably 7.5 percent, compared to the comparative complex. Highly preferably, the average value of all bond angles, Θ, is also less than in the comparative complex.

Preferably, monocyclopentadienyl metal coordination complexes of group 4 or lanthanide metals according to the present invention have constrained geometry such that the smallest angle, Θ, is less than 115°, more preferably less than 110°, most preferably less than 105°.

Other compounds which are useful in the catalyst compositions of this invention, especially compounds containing other Group 4 or Lanthanide metals, will, of course, be apparent to those skilled in the art.

In general, the polymerization according to the present invention may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0° to 250° C. and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired. A support may be employed but preferably the catalysts are used in a homogeneous manner. It will, of course, be appreciated that the active catalyst system, especially nonionic catalysts, form in situ if the catalyst and the cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

The polymerization conditions for manufacturing the polymers of the present invention are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Fabricated articles made from the novel olefin polymers may be prepared using all of the conventional polyolefin processing techniques. Useful articles include films (e.g., cast, blown and extrusion coated), fibers (e.g., staple fibers (include-nu use of a novel olefin polymer disclosed herein as at least one component comprising at least a portion of the fiber's surface), spunbond fibers or melt blown fibers (using, e.g., systems as disclosed in U.S. Pat. No. 4,430,563, U.S. Pat. No. 4,663,220, U.S. Pat. No. 4,668,566, or U.S. Pat. No. 4,322,027, all of which are incorporated herein by reference), and gel spun fibers (e.g., the system disclosed in U.S. Pat. No. 4,413,110, incorporated herein by reference)), both woven and nonwoven fabrics (e.g., spunlaced fabrics disclosed in U.S. Pat. No. 3,485,706, incorporated herein by reference) or structures made from such fibers (including, e.g., blends of these fibers with other fibers, e.g., PET or cotton) and molded articles (e.g., made using an injection molding process, a blow molding process or a rotomolding process). The new polymers described herein are also useful for wire and cable coating operations, as well as in sheet extrusion for vacuum forming operations.

Useful compositions are also suitably prepared comprising the substantially linear polymers of the present invention and at least one other natural or synthetic polymer. Preferred other polymers include thermoplastics such as styrene-butadiene block copolymers, polystyrene (including high impact polystyrene), ethylene vinyl alcohol copolymers, ethylene acrylic acid copolymers, other olefin copolymers (especially polyethylene copolymers) and homopolymers (e.g., those made using conventional heterogeneous catalysts). Examples include polymers made by the process of U.S. Pat. No. 4,076,698, incorporated herein by reference, other linear or substantially linear polymers of the present invention, and mixtures thereof. Other substantially linear polymers of the present invention and conventional HDPE and/or LLDPE are preferred for use in the thermoplastic compositions.

Compositions comprising the olefin polymers can also be formed into fabricated articles such as those previously mentioned using conventional polyolefin processing techniques which are well known to those skilled in the art of polyolefin processing.

All procedures were performed under an inert atmosphere or nitrogen or argon. Solvent choices were often optional, for example, in most cases either pentane or 30–60 petroleum ether can be interchanged. Amines, silanes, lithium reagents, and Grignard reagents were purchased from Aldrich Chemical Company. Published methods for preparing tetramethylcyclopentadiene ($C_5Me_4H_2$) and lithium tetramethylcyclopentadienide ($Li(C_5Me_4H)$) include C. M. Fendrick et al. *Organometallics*, 3, 819 (1984). Lithiated substituted cyclopentadienyl compounds may be typically prepared from the corresponding cyclopentadiene and a lithium reagent such as n-butyl lithium. Titanium trichloride ($TiCl_3$) was purchased from Aldrich Chemical Company. The tetrahydrofuran adduct of titanium trichloride, $TiCl_3(THF)_3$, was prepared by refluxing $TiCl_3$ in THF

overnight, cooling, and isolating the blue solid product, according to the procedure of L. E. Manzer, *Inorg. Syn.*, 21, 135 (1982).

EXAMPLES 1-4

The metal complex solution for Example 1 is prepared as follows:

Part 1: Prep of $Li(C_5Me_4H)$

In the drybox, a 3 L 3-necked flask was charged with 18.34 g of $C_5Me_4H_2$, 800 mL of pentane, and 500 mL of ether. The flask was topped with a reflux condenser, a mechanical stirrer, and a constant addition funnel container 63 mL of 2.5M n-BuLi 4Ln hexane. The BuLi was added dropwise over several hours. A very thick precipitate formed: approx. 1000 mL of additional pentane had to be added over the course of the reaction to allow stirring to continue. After the addition was complete, the mixture was stirred overnight. The next day, the material was filtered, and the solid was thoroughly washed with pentane and then dried under reduced pressure. 14.89 g of $Li(C_5Me_4H)$ was obtained (78 percent).

Part 2: Prep of $C_5Me_4HSiMe_2Cl$

In the drybox 30.0 g of $Li(C_5Me_4H)$ was placed in a 500 mL Schlenk flask with 250 mL of THF and a large magnetic stir bar. A syringe was charged with 30 mL of Me_2SiCl_2 and the flask and syringe were removed from the drybox. On the Schlenk line under a flow of argon, the flask was cooled to −78° C., and the Me_2SiCl_2 added in one rapid addition. The reaction was allowed to slowly warm to room temperature and stirred overnight. The next morning the volatile materials were removed under reduced pressure, and the flask was taken into the drybox. The oily material was extracted with pentane, filtered, and the pentane was removed under reduced pressure to leave the $C_5Me_4HSiMe_2Cl$ as a clear yellow liquid (46.83 g; 92.9 percent).

Part 3: Prep of $C_5Me_4HSiMe_2NH^tBu$

In the drybox, a 3-necked 2 L flask was charged with 37.4 g of t-butylamine and 210 mL of THF. C_5Me_4H-$SiMe_2Cl$ (25.47 g) was slowly dripped into the solution over 3–4 hours. The solution turned cloudy and yellow. The mixture was stirred overnight and the volatile materials removed under reduced pressure. The residue was extracted with diethyl ether, the solution was filtered, and the ether removed under reduced pressure to leave the $C_5Me_4HSiMe_2NH^tBu$ as a clear yellow liquid (26.96 g; 90.8 percent).

Part 4: Prep $[MgCl]_2[Me_4C_5SiMe_2N^tBu](THF)_x$

In the drybox, 14.0 mL of 2.0M isopropylmagnesium chloride in ether was syringed into a 250 mL flask. The ether was removed under reduced pressure to leave a colorless oil. 50 mL of a 4:1 (by volume) toluene:THF mixture was added followed by 3.50 g of $Me_4HC_5SiMe_2NH^tBU$. The solution was heated to reflux. After refluxing for 2 days, the solution was cooled and the volatile materials removed under reduced pressure. The white solid residue was slurried in pentane and filtered to leave a white powder, which was washed with pentane and dried under reduced pressure. The white powder was identified as $[MgCl]_2[Me_4C_5SiMe_2N^tBu](THF)_x$ (yield: 6.7 g).

Part 5: Prep of $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$

In the drybox, 0.50 g of $TiCl_3(THF)_3$ was suspended in 10 mL of THF. 0.69 g of solid $[MgCl]_2[Me_4C_5SiMe_2N^tBu](THF)_x$ was added, resulting in a color change from pale blue to deep purple. After 15 minutes, 0.35 g of AgCl was added to the solution. The color immediately began to lighten to a pale green-yellow. After 1½ hours, the THF was removed under reduced pressure to leave a yellow-green solid. Toluene (20 mL) was added, the solution was filtered, and the toluene was removed under reduced pressure to leave a yellow-green solid, 0.51 g (quantitative yield) identified by 1H NMR as $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$.

Part 6: Preparation of $[C_5Me_4(SiMe_2N^tBu)]TiMe_2$

In an inert atmosphere glove box, 9.031 g of $[C_5Me_4(Me_2SiN^tBu)]TiCl_2$ is charged into a 250 ml flask and dissolved into 100 ml of THF. This solution is cooled to about −25° C. by placement in the glove box freezer for 15 minutes. To the cooled solution is added 35 ml of a 1.4M MeMgBr solution in toluene/THF (75/25). The reaction mixture is stirred for 20 to 25 minutes followed by removal of the solvent under vacuum. The resulting solid is dried under vacuum for several hours. The product is extracted with pentane (4×50 ml) and filtered. The filtrate is combined and the pentane removed under vacuum giving the catalyst as a straw yellow solid.

The metal complex, $[C_5Me_4(SiMe_2N^tBu)]TiMe_2$, solution for Examples 2 and 3 is prepared as follows:

In an inert atmosphere glove box 10.6769 g of a tetrahydrofuran adduct of titanium trichloride, $TiCl_3(THF)_3$, is loaded into a 1 l flask and slurried into ≈300 ml of THF. To this slurry, at room temperature, is added 17.402 g of $[MgCl]_2[N^tBuSiMe_2C_5Me_4]$ $(THF)_x$ as a solid. An additional 200 ml of THF is used to help wash this solid into the reaction flask. This addition resulted in an immediate reaction giving a deep purple solution. After stirring for 5 minutes 9.23 ml of a 1.56M solution of CH_2Cl_2 in THF is added giving a quick color change to dark yellow. This stage of the reaction is allowed to stir for about 20 to 30 minutes. Next, 61.8 m l of a 1.4M MeMgBr solution in toluene/THF(75/25) is added via syringe. After about 20 to 30 minutes stirring tame the solvent is removed under vacuum and the solid dried. The product is extracted with pentane (8×50 ml) and filtered. The filtrate is combined and the pentane removed under vacuum giving the metal complex as a tan solid.

The metal complex, $[C_5Me_4(SiMe_2N^tBu)]TiMe_2$, solution for Example 4 is prepared as follows:

In an inert atmosphere glove box 4.8108 g of $TiCl_3(thf)_3$ is placed in a 500 ml flask and slurried into 130 ml of THF. In a separate flask 8.000 g of $[MgCl]_2[N^tBuSiMe_2C_5Me_4](THF)_x$ is dissolved into 150 ml of THF. These flasks are removed from the glove box and attached to a vacuum line and the contents cooled to −30° C. The THF solution of $[MgCl]_2[N^tBuSiMe_2C_5Me_4](THF)_x$ is transferred (over a 15 minute period) via cannula to the flask containing the $TiCl_3(THF)_3$ slurry. This reaction is allowed to stir for 1.5 hours over which time the temperature warmed to 0° C. and the solution color turned deep purple. The reaction mixture is cooled back to −30° C. and 4.16 ml of a 1.56M CH_2Cl_2 solution in THF is added. This stage of the reaction is stirred for an additional 1.5 hours and the temperature warmed to −10° C. Next, the reaction mixture is again cooled to −40° C. and 27.81 ml of a 1.4M MeMgBr solution in toluene/THF (75/25) was added via syringe and the reaction is now allowed to warm slowly to room temperature over 3 hours. After this time the solvent is removed under vacuum and the solid dried. At this point the reaction flask is brought back into the glove box where the product is extracted

with pentane (4×50 ml) and filtered. The filtrate is combined and the pentane removed under vacuum giving the catalyst as a tan solid. The metal complex is then dissolved into a mixture of C_8–C_{10} saturated hydrocarbons (e.g., Isopar ® E, made by Exxon) and ready for use in polymerization.

Polymerization

The polymer products of Examples 1–4 are produced in a solution polymerization process using a continuously stirred reactor. Additives (e.g., antioxidants, pigments, etc.) can be incorporated into the interpolymer products either during the pelletization step or after manufacture, with a subsequent re-extrusion. Examples 1–4 are each stabilized with 1250 ppm Calcium Stearate, 200 ppm IRGANOX 1010, and 1600 ppm Irgafos 168, Irgafos ™ 168 is a phosphite stabilizer and IRGANOX ™ 1010 is a hindered polyphenol stabilizer (e.g., tetrakis [methylene 3-(3,5-ditert.butyl-4-hydroxyphenylpropionate)]methane. Both are trademarks of and made by Ciba-Geigy Corporation. A representative schematic for the polymerization process is shown in FIG. 1.

The ethylene (4) and the hydrogen are combined into one, stream (15) before being introduced into the diluent mixture (3). Typically, the diluent mixture comprises a mixture of C_8–C_{10} saturated hydrocarbons (1), (e.g., Isopar ® E, made by Exxon) and the comonomer(s) (2). For examples 1–4, the comonomer is 1-octene. The reactor feed mixture (6) is continuously injected into the reactor (9). The metal complex (7) and the cocatalyst (8) (the cocatalyst is tris(pentafluorophenyl)borane for Examples 1–4 herein which forms the ionic catalyst insitu) are combined into a single stream and also continuously injected into the reactor. Sufficient residence time is allowed for the metal complex and cocatalyst to react to the desired extent for use in the polymerization reactions, at least about 10 seconds. For the polymerization reactions of Examples 1–4. the reactor pressure is held constant at about 490 psig. Ethylene content of the reactor, after reaching steady state, is maintained below about 8 percent.

After polymerization, the reactor exit stream (14) is introduced into a separator (10) where the molten polymer is separated from the unreacted comonomer(s), unreacted ethylene, unreacted hydrogen, and diluent mixture stream (13). The molten polymer is subsequently strand chopped or pelletized and, after being cooled in a water bath or pelletizer (11), the solid pellets are collected (12). Table I describes the polymerization conditions and the resultant polymer properties:

TABLE I

Example	1	2	3	4
Ethylene feed rate (lbs/hour)	3.2	3.8	3.8	3.8
Comonomer/ Olefin* ratio (mole %)	12.3	0	0	0
Hydrogen/ Ethylene ratio (mole %)	0.054	0.072	0.083	0.019
Diluent/ Ethylene ratio (weight basis)	9.5	7.4	8.7	8.7
metal complex concentration (molar)	0.00025	0.0005	0.001	0.001
metal complex flow rate (ml/min)	5.9	1.7	2.4	4.8
cocatalyst concentration (molar)	0.001	0.001	0.002	0.002
cocatalyst flow rate (ml/min)	2.9	1.3	6	11.9
Reactor temperature (°C.)	114	160	160	200
Ethylene Conc. in the reactor exit steam (weight percent)	2.65	3.59	0.86	1.98
Product I_2 (g/10 minutes)	1.22	0.96	1.18	0.25
Product density (g/cc)	0.903	0.954	0.954	0.953
Product I_{10}/I_2	6.5	7.4	11.8	16.1
Product M_w/M_n	1.86	1.95	2.09	2.07

*For Examples 1–4, the Comonomer/Olefin ratio is defined as the percentage molar ratio of ((1-octene/(1-octene + ethylene))

The ^{13}C NMR spectrum of Example 3 (ethylene homopolymer) shows peaks which can be assigned to the $\alpha\delta+$, $\beta\delta+$, and methine carbons associated with a long chain branch. Long chain branching is determined using the method of Randall described earlier in this disclosure, wherein he states that "Detection of these resonances in high-density polyethylenes where no 1-olefins were added during the polymerization should be strongly indicative of the presence of long chain branching." Using the equation 141 from Randall (p. 292):

$$\text{Branches per 10,000 carbons} = [\frac{1}{3}\alpha/T_{Tot}] \times 10^4,$$

wherein α = the average intensity of a carbon from a branch ($\alpha\delta+$) carbon and T_{Tot} = the total carbon intensity,

the number of long chain branches in this sample is determined to be 3.4 per 10,000 carbon atoms, or 0.34 long chain branches/1000 carbon atoms.

EXAMPLES 5, 6 and COMPARATIVE EXAMPLES 7–9

Examples 5, 6 and comparison examples 7–9 with the same melt index are tested for rheology comparison. Examples 5 and 6 are the substantially linear polyethylenes produced by the constrained geometry catalyst technology, as described in Examples 1–4. Examples 5 and 6 are stablized as Examples 1–4.

Comparison examples 7, 8 and 9 are conventional heterogeneous Ziegler polymerization blown film resins Dowlex ® 2045A, Attane ® 4201, and Attane ® 4403, respectively, all of which are ethylene/1-octene copolymers made by The Dow Chemical Company. Comparative example 7 is stablized with 200 ppm IRGANOX ® 1010, and 1600 ppm Irgafos ® 168 while comparative examples 8 and 9 are stablized with 200 ppm IRGANOX ® 1010 and 800 ppm PEPQ ®. PEPQ ® is a trademark of Sandoz Chemical, the primary ingredient of which is believed to be tetrakis-(2,4-di-tertbutylphenyl)-4,4' biphenylphosphonite.

A comparison of the physical properties of each example and comparative example is listed in Table II.

TABLE II

Property	Example 5	Example 6	Comparison Example 7	Comparison Example 8	Comparison Example 9
I_2	1	1	1	1	0.76
density	.92	.902	.92	.912	.905
I_{10}/I_2	9.45	7.61	7.8–8	8.2	8.7
M_w/M_n	1.97	2.09	3.5–3.8	3.8	3.8–4.0

Surprisingly, even though the molecular weight distribution of Examples 5 and 6 is narrow (i.e., M_w/M_n is low), the I_{10}/I_2 values are higher in comparison with comparative examples 7–9. A comparison of the relationship between I_{10}/I_2 vs. M_w/M_n for some of the novel polymers described herein and conventional heterogeneous Ziegler polymers is given in FIG. 2. The I_{10}/I_2 value for the novel polymers of the present invention is essentially independent of the molecular weight distribution, M_w/M_n, which is not true for conventional Ziegler polymerized resins.

Example 5 and comparison example 7 with similar melt index and density (Table II) are also extruded via a Gas Extrusion Rheometer (GER) at 190° C. using a 0.0296" diameter, 20 L/D die. The processing index (P.I.) is measured at an apparent shear stress of 2.15×10^6 dyne/cm^2 as described previously. The onset of gross melt fracture can easily be identified from the shear stress vs. shear rate plot shown in FIG. 3 where a sudden jump of shear rate occurs. A comparison of the shear stresses and corresponding shear rates before the onset of gross melt fracture is listed in Table III. It is particularly interesting that the PI of Example 5 is more than 20% lower than the PI of comparative example 7 and that the onset of melt fracture or sharkskin for Example 5 is also at a significantly higher shear stress and shear rate in comparison with the comparative example 7. Furthermore, the Melt Tension (MT) as well as Elastic Modulus of Example 5 are higher than that of comparative example 7.

TABLE III

Property	Example 5	Comparison example 7
I_2	1	1
I_{10}/I_2	9.45	7.8–8
PI, kpoise	11	15
Melt Tension	1.89	1.21
Elastic Modulus @.1 rad/sec. (dyne/cm^2)	2425	882.6
OGMF*, critical shear rate (1/sec)	>1556 (not observed)	936
OGMF*, critical shear stress (MPa)	.452	.366
OSMF**, critical shear rate (1/sec.)	>1566 (not observed)	~628
OSMF**, critical shear stress (MPa)	~0.452	~0.25

*Onset of Gross Melt Fracture.
**Onset of Surface Melt Fracture.

Example 6 and comparison example 9 have similar melt index and density, but example 6 has lower I_{10}/I_2 (Table IV). These polymers are extruded via a Gas Extrusion Rheometer (GER) at 190° C. using a 0.0296 inch diameter, 20:1 L/D die. The processing index (PI) is measured at an apparent shear stress of 2.15×10^6 dyne/cm^2 as described previously.

TABLE IV

Property	Example 6	Comparison example 9
I_2(g/10 minutes)	1	0.76
I_{10}/I_2	7.61	8.7
PI (kpoise)	14	15
Melt Tension (g)	1.46	1.39
Elastic Modulus @ 0.1 rad/sec (dyne/cm2)	1481	1921
OGMF*, critical shear rate (1/sec)	1186	652
OGMF*, critical shear stress (MPa)	0.431	0.323
OSMF**, critical shear rate (1/sec.)	~764	~402
OSMF**, critical shear stress (MPa)	0.366	0.280

*Onset of Gross Melt Fracture.
**Onset of Surface Melt Fracture.

The onset of gross melt fracture can easily be identified from the shear stress vs. shear rate plot shown in FIG. 4 where a sudden increase of shear rate occurs at an apparent shear stress of about 3.23×10^6 dyne/cm^2 (0.323 Mpa). A comparison of the shear stresses and corresponding shear rates before the onset of gross melt fracture is listed in Table IV. The PI of Example 6 is surprisingly about the same as comparative example 9, even though the I_{10}/I_2 is lower for Example 6. The onset of melt fracture or sharkskin for Example 6 is also at a significantly higher shear stress and shear rate in comparison with the comparative example 9. Furthermore, it is also unexpected that the Melt Tension (MT) of Example 6 is higher than that of comparative example 9, even though the melt index for Example 6 is slightly higher and the I_{10}/I_2 is slightly lower than that of comparative example 9.

EXAMPLE 10 AND COMPARATIVE EXAMPLE 11

Blown film is fabricated from two novel ethylene/1-octene polymers made in accordance with the present invention and from two comparative conventional polymers made according to conventional Ziegler catalysis. The blown films are tested for physical properties, including heat seal strength versus heat seal temperature (shown in FIG. 5 for Examples 10 and 12 and comparative examples 11 and 13). machine (MD) and cross direction (CD) properties (e.g., tensile yield and break, elongation at break and Young's modulus). Other film properties such as dart, puncture, tear, clarity, haze, 20 degree gloss and block are also tested.

Blown Film Fabrication Conditions

The improved processing substantially linear polymers of the present invention produced via the procedure described earlier, as well as two comparative resins are fabricated on an Egan blown film line using the following fabrication conditions:

2 inch extruder
3 inch die
30 mil die gap

25 RPM extruder speed
460° F. melt temperature
1 mil gauge
2.7:1 Blow up ratio (12.5 inches layflat)
12.5 inches frost line height

The melt temperature is kept constant by changing the extruder temperature profile. Frost line height is maintained at 12.5 inches by adjusting the air flow. The extruder output rate, back pressure and power consumption in amps are monitored throughout the experiment. The polymers of the present invention and the comparative polymers are all ethylene/1-octene copolymers. Table VI summarizes physical properties of the two polymers of the invention and for the two comparative polymers:

TABLE VI

Property	Example 10	Comparative example 11	Example 12	Comparative example 13
I_2 (g/10 minutes)	1	1	1	0.8
Density (g/cc)	0.92	0.92	0.902	0.905
I_{10}/I_2	9.45	~8	7.61	8.7
M_w/M_n	2	~5	2	~5

Tables VII and VIII summarize the film properties measured for blown film made from two of these four polymers:

TABLE VII

	Blown film properties			
	Example 10		Comparative example 11	
Property	MD	CD	MD	CD
Tensile yield (psi)	1391	1340	1509	1593
Tensile break (psi)	7194	5861	6698	6854
elongation (percent)	650	668	631	723
Young's Modulus (psi)	18990	19997	23086	23524
PPT* Tear (gm)	5.9	6.8	6.4	6.5

*Puncture Propagation Tear

TABLE VIII

Property	Example 10	Comparative example 11
Dart A (gm)	472	454
Puncture (grams)	235	275
clarity (percent)	71	68
Haze	3.1	6.4
20° gloss	114	81
Block (grams)	148	134

During the blown film fabrication, it is noticed that at the same screw speed (25 rpm) and at the same temperature profile, the extruder back pressure is about 3500 psi at about 58 amps power consumption for comparative example 11 and about 2550 psi at about 48 amps power consumption for example 10, thus showing the novel polymer of example 10 to have improved processability over that of a conventional heterogeneous Ziegler polymerized polymer. The throughput is also higher for Example 10 than for comparative example 11 at the same screw speed. Thus, example 10 has higher pumping efficiency than comparative example 11 (i.e., more polymer goes through per turn of the screw).

As FIG. 5 shows, the heat seal properties of polymers of the present invention are improved, as evidenced by lower heat seal initiation temperatures and higher heat seal strengths at a given temperature, as compared with conventional heterogeneous polymers at about the same melt index and density.

What is claimed is:

1. A substantially linear olefin polymer characterized as having:

a) a melt flow ratio, I_{10}/I_2, $\geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2,

wherein the olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

2. The polymer of claim 1 wherein the M_w/M_n is less than about 3.5.

3. The polymer of claim 1 wherein the M_w/M_n is from about 1.5 to about 2.5.

4. The polymer of claim 1 wherein the polymer has about 0.01 to about 3 long chain branches/1000 carbons along the polymer backbone.

5. The polymer of claim 4 having at least about 0.1 long chain branches/1000 carbons along the polymer backbone.

6. The polymer of claim 4 having at least about 0.3 long chain branches/1000 carbons along the polymer backbone.

7. A composition comprising a substantially linear olefin polymer, wherein the polymer is characterized as having:

a) a melt flow ratio, I_{10}/I_2, $\geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2,

and at least one other natural or synthetic polymer, wherein the substantially linear olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

8. The composition of claim 7 wherein the substantially linear olefin polymer has a I_{10}/I_2 up to about 20.

9. The composition of claim 7 wherein the substantially linear olefin polymer has a M_w/M_n less than about 3.5.

10. The composition of claim 7 wherein the substantially linear olefin polymer has a M_w/M_n from about 1.5 to about 2.5.

11. The composition of claim 7 wherein the synthetic polymer is a conventional ethylene homopolymer or copolymer.

12. A substantially linear olefin polymer having a melt flow ratio, I_{10}/I_2, $\leqq 5.63$, and a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63,$$

produced by continuously contacting ethylene and a C_3–C_{20} alpha-olefin with a catalyst composition under

polymerization conditions, wherein said catalyst composition is characterized as:

a) a metal coordination complex comprising a metal atom of groups 3–10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized π-bonded moiety substituted with a constrain inducing moiety,

said complex having a constrained geometry about the metal atom such that the angle at the metal atom between the centroid of the delocalized, substituted π-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π-bonded moiety lacking in such constrain-inducing substituent,

and provided further that for such complexes comprising more than one delocalized, substituted π-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π-bonded moiety, and

b) an activating cocatalyst.

13. A substantially linear olefin polymer characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≧7,

b) a molecular weight distribution, M_w/M_n, of from about 1.5 to about 2.5,

wherein the substantially linear olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

14. The polymer of claim **13** wherein the I_{10}/I_2 is at least about 8.

15. The polymer of claim **13** wherein the I_{10}/I_2 is at least about 9.

16. The polymer of claim **13** wherein the substantially linear olefin polymer is an ethylene/alpha-olefin copolymer.

17. A substantially linear olefin polymer having:

(a) from about 0.01 to about 3 long chain branches/1000 carbons along the polymer backbone and

(b) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2,

wherein the substantially linear olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

18. The polymer of claim **17** having at least about 0.1 long chain branches/1000 carbons along the polymer backbone.

19. The polymer of claim **17** having at least about 0.3 long chain branches/1000 carbons along the polymer backbone.

20. The polymer of claim **17** wherein the polymer has a I_{10}/I_2 of at least about 16.

21. The substantially linear olefin polymer of claim **1**, wherein the polymer is a copolymer of ethylene and 1-octene.

22. The substantially linear olefin polymer of claim **1**, wherein the polymer is a copolymer of ethylene and 1-hexene.

23. The substantially linear olefin polymer of claim **1**, wherein the polymer is a copolymer of ethylene and 1-butene.

24. The substantially linear olefin polymer of claim **1**, wherein the polymer is a copolymer of ethylene and 4-methyl-1-pentene.

25. The composition of claim **7**, wherein the substantially linear olefin polymer is a copolymer of ethylene and 1-octene.

26. The composition of claim **7**, wherein the substantially linear olefin polymer is a copolymer of ethylene and 1-hexene.

27. The composition of claim **7**, wherein the substantially linear olefin polymer is a copolymer of ethylene and 1-butene.

28. The composition of claim **7**, wherein the substantially linear olefin polymer is a copolymer of ethylene and 4-methyl-1-pentene.

29. The substantially linear olefin polymer of claim **13**, wherein the polymer is a copolymer of ethylene and 1-octene.

30. The substantially linear olefin polymer of claim **13**, wherein the polymer is a copolymer of ethylene and 1-hexene.

31. The substantially linear olefin polymer of claim **13**, wherein the polymer is a copolymer of ethylene and 1-butene.

32. The substantially linear olefin polymer of claim **13**, wherein the polymer is a copolymer of ethylene and 4-methyl-1-pentene.

33. The substantially linear olefin polymer of claim **17**, wherein the polymer is a copolymer of ethylene and 1-octene.

34. The substantially linear olefin polymer of claim **17**, wherein the polymer is a copolymer of ethylene and 1-hexene.

35. The substantially linear olefin polymer of claim **17**, wherein the polymer is a copolymer of ethylene and 1-butene.

36. The substantially linear olefin polymer of claim **17**, wherein the polymer is a copolymer of ethylene and 4-methyl-1-pentene.

37. A composition comprising:

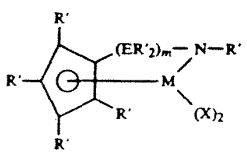
(i) a substantially linear olefin polymer, wherein the substantially linear olefin polymer is characterized as having:

a) from about 0.01 to about 3 long chain branches/1000 carbons along the polymer backbone and

b) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2, and

(ii) at least one other natural or synthetic polymer, wherein the substantially linear olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

38. The substantially linear olefin polymer of claim **12** wherein (a) is an amidosilane- or amidoalkanediyl- compound corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, or aryl, of up to 20 carbons; and

m is 1 or 2.

* * * * *

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CCC48 XR 5,272,236

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,272,236 Page 1 of 5
DATED : December 21, 1993
INVENTOR(S) : Shih-Yaw Lai et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

On the cover page, under Other Publications, after pp. 2869-2880, "(1993))," should read --(1963))),--.

On page 2, under Other Publications, first column, Makromol. Chem. Rapid Commun., in the title, "Aluminoxiane" " should read --Aluminoxane"--.

On page 2, under Other Publications, first column, Journal of Polymer Science, in the title "Transaction" should be --Transition--.

On page 2, under Other Publications, second column, Makromol. Chem. Commun., in the title "Zicronocene" should read --Zirconocene--.

On drawing sheet

In Fig.5, the "dashed line" describing peel strength between 215°F and 225°F for Comparative Example 11 should be a --solid line--.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,272,236

DATED : December 21, 1993

INVENTOR(S) : Shih-Yaw Lai et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 4, line 59, "an" should read -- a --.

Column 5, line 35, "(R)" should read -- Σ --.

Column 7, line 42, "a" should read -- as --.

Column 7, line 64, "-N(R"-" should read -- -N(R")- --.

Column 7, line 15, "51" should read -- M --.

Column 8, line 40, "ramethyl-η^5-cydoperitadienyl)-1,2-ethanediyltitanium" should read - - ramethyl-η^5-cydopentadienyl)-1,2-ethanediyltitanium - -.

Column 10, line 65, "Rot" should read -- not --.

Column 11, line 11, "(L-H)$^+$[A]" should read -- (L-H)$^+$[A]$^-$ --.

Column 11, line 35, "[L-H]$^+$[BQ4]" should read -- [L-H]$^+$[BQ4]$^-$ --.

Column 12, line 36, "Cp" should read -- Cp* --.

Column 12, line 59, "Tris(pentafluorphenyl)borane" should read -- Tris(pentafluorophenyl)borane --.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : **5,272,236**

DATED : **December 21, 1993**

INVENTOR(S) : **Shih-Yaw Lai et al.**

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 13, line 11, "η-bonding" should read -- π-bonding --.

Column 14, line 12, "include-nu" should read -- including --.

Column 14, line 54 (1st instance), "or" should read -- of --.

Column 15, line 13, "tainer" should read -- taining --.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,272,236
DATED : December 21, 1993
INVENTOR(S) : Shih-Yaw Lai et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 15, line 13, "4Ln" should read -- in --.

Column 15, line 49, "Prep [MgCl]2[Me4C5Si Me2N^{t}Bu](THF)$_x$" should read -- Prep of [MgCl]2[Me4C5Si Me2N^{t}Bu](THF)$_x$ --.

Column 15, line 55, in the formula "BU" should read -- Bu --.

Column 16, line 36, "m l" should read -- ml --.

Column 16, line 47, "TiCl3(thf)3" should read -- TiCl3(THF)3 --.

Column 17, line 14, "Calcium Stearate" should read -- calcium stearate --.

Column 17, line 34, "Insitu" should read -- *in situ* --.

Column 18, line 15, "exit steam" should read -- exit stream --.

Column 20, line 32, "(0.323 Mpa)" should read -- (0.323 MPa) --.

Column 20, line 55, "examples 11 and 13)." should read -- examples 11 and 13), --.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : **5,272,236** Page 5 of 5

DATED : **December 21, 1993**

INVENTOR(S) : **Shih-Yaw Lai et al.**

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 22, line 62, "≦" should read -- ≥ --.

Column 16, line 37, "tame" should read -- time --.

Column 17, line 15, "1600 ppm Irgafos 168," should read -- 1600 ppm Irgafos 168. --.

Column 17, line 25, "one, stream" should read -- one stream --.

Signed and Sealed this

Twenty-ninth Day of November, 1994

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

US005278272A

United States Patent [19]

Lai et al.

[11] Patent Number: 5,278,272

[45] Date of Patent: Jan. 11, 1994

[54] **ELASTIC SUBSTANTIALY LINEAR OLEFIN POLYMERS**

[75] Inventors: **Shih-Yaw Lai**, Sugar Land; **John R. Wilson**, Richwood; **George W. Knight**, Lake Jackson, all of Tex.; **James C. Stevens**, Midland, Mich.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **939,281**

[22] Filed: **Sep. 2, 1992**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 776,130, Oct. 15, 1991.

[51] **Int. Cl.**[5] **C08F 10/04**; C08F 210/02; C08F 210/14

[52] **U.S. Cl.** **526/348.5**; 526/348; 526/348.1; 526/348.2; 526/348.3; 526/348.4; 526/348.6; 526/348.7

[58] **Field of Search** 526/170, 348, 348.2, 526/348.3, 348.4, 348.5, 348.6, 348.7, 348.1

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Primary Examiner—Joseph L. Schofer
Assistant Examiner—David Wu
Attorney, Agent, or Firm—Stephen P. Krupp; L. Wayne White

[57] **ABSTRACT**

Elastic substantially linear olefin polymers are disclosed which have very good processability, including processing indices (PI's) less than or equal to 70 percent of those of a comparative linear olefin polymer and a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a traditional linear olefin polymer at about the same I_2 and M_w/M_n. The novel polymers have higher low/zero shear viscosity and lower high shear viscosity than comparative linear olefin polymers.

37 Claims, 1 Drawing Sheet

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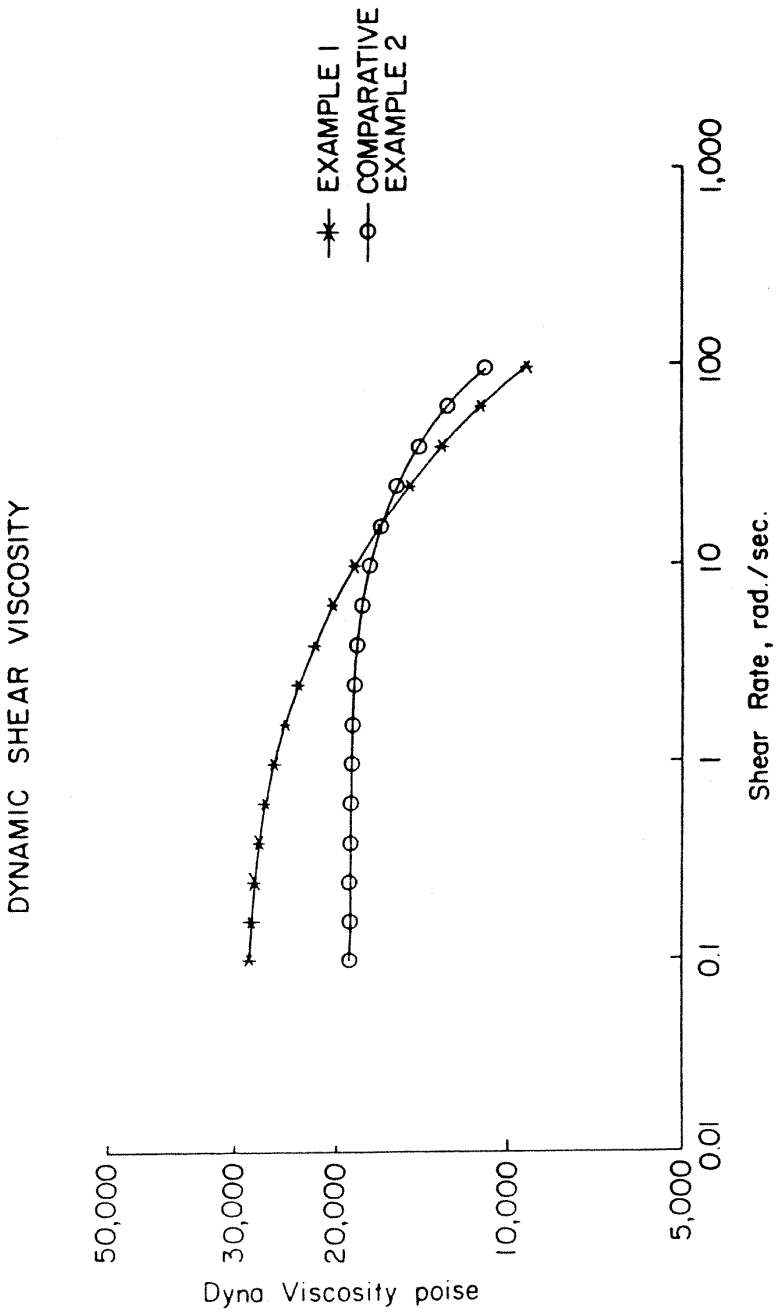
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FIG. 1


DYNAMIC SHEAR VISCOSITY
EXAMPLE 1
COMPARATIVE EXAMPLE 2
50,000
30,000
20,000
10,000
5,000
Dyna Viscosity poise
0.01
0.1
1
10
100
1,000
Shear Rate, rad./sec.

ELASTIC SUBSTANTIALY LINEAR OLEFIN POLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part of pending application Ser. No. 07/776,130, filed Oct. 15, 1991, pending the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to elastic substantially linear olefin polymers having improved processability, e.g., low susceptibilty to melt fracture, even under high shear stress conditions. Such substantially linear ethylene polymers have a critical shear rate at the onset of surface melt fracture substantially higher than, and a processing index substantially less than, that of a linear polyethylene at the same molecular weight distribution and melt index.

BACKGROUND OF THE INVENTION

Molecular weight distribution (MWD), or polydispersity, is a well known variable in polymers. The molecular weight distribution, sometimes described as the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) (i.e., M_w/M_n) can be measured directly, e.g., by gel permeation chromatography techniques, or more routinely, by measuring I_{10}/I_2 ratio, as described in ASTM D-1238. For linear polyolefins. especially linear polyethylene, it is well known that as M_w/M_n increases, I_{10}/I_2 also increases.

John Dealy in "Melt Rheology and Its Role in Plastics Processing" (Van Nostrand Reinhold, 1990) page 597 discloses that ASTM D-1238 is employed with different loads in order to obtain an estimate of the shear rate dependence of melt viscosity, which is sensitive to weight average molecular weight (M_w) and number average molecular weight (M_n).

Bersted in Journal of Applied Polymer Science Vol. 19, page 2167–2177 (1975) theorized the relationship between molecular weight distribution and steady shear melt viscosity for linear polymer systems. He also showed that the broader MWD material exhibits a higher shear rate or shear stress dependency.

Ramamurthy in *Journal of Rheology*, 30(2), 337–357 (1986), and Moynihan, Baird and Ramanathan in Journal of Non-Newtonian Fluid Mechanics, 36, 255–263 (1990), both disclose that the onset of sharkskin (i.e., melt fracture) for linear low density polyethylene (LLDPE) occurs at an apparent shear stress of 1–1.4 × 106 dyne/cm^2, which was observed to be coincident with the change in slope of the flow curve. Ramamurthy also discloses that the onset of surface melt fracture or of gross melt fracture for high pressure low density polyethylene (HP-LDPE) occurs at an apparent shear stress of about 0.13 MPa (1.3×10^6 dynes/cm^2).

Kalika and Denn in *Journal of Rheology*, 31, 815–834 (1987) confirmed the surface defects or sharkskin phenomena for LLDPE, but the results of their work determined a critical shear stress of 2.3×10^6 dyne/cm^2, significantly higher than that found by Ramamurthy and Moynihan et al. International Patent Application (Publication No. WO 90/03414) published Apr. 5, 1990, discloses linear ethylene interpolymer blends with narrow molecular weight distribution and narrow short chain branching distributions (SCBDs). The melt processibility of the interpolymer blends is controlled by blending different molecular weight interpolymers having different narrow molecular weight distributions and different SCBDs.

Exxon Chemical Company, in the Preprints of Polyolefins VII International Conference, page 45–66, Feb. 24–27 1991, disclose that the narrow molecular weight distribution (NMWD) resins produced by their EXXPOL TM technology have higher melt viscosity and lower melt strength than conventional Ziegler resins at the same melt index. In a recent publication, Exxon Chemical Company has also taught that NMWD polymers made using a single site catalyst create the potential for melt fracture ("New Specialty Linear Polymers (SLP) For Power Cables," by Monica Hendewerk and Lawrence Spenadel, presented at IEEE meeting in Dallas, Tex., September, 1991).

Previously known narrow molecular weight distribution linear polymers disadvantageously possessed low shear sensitivity or low I_{10}/I_2 value, which limits the extrudability of such polymers. Additionally, such polymers possessed low melt elasticity, causing problems in melt fabrication such as film forming processes or blow molding processes (e.g., sustaining a bubble in the blown film process, or sag in the blow molding process etc.). Finally, such resins also experienced melt fracture surface properties at relatively low extrusion rates thereby processing unacceptably.

SUMMARY OF THE INVENTION

Elastic substantially linear olefin polymers have now been discovered which have unusual properties, including an unusual combination of properties, which leads to enhanced processability of the novel polymers. The substantially linear olefin polymers have the process ability similar to highly branched low density polyethylene, but the strength in toughness of linear low density polyethylene. The substantially linear olefin polymer are characterized as having a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n.

The elastic substantially linear olefin polymers also have a processing index (PI) less than or equal to about 70% of the PI of a comparative linear olefin polymer at about the same I_2 and M_w/M_n.

The elastic substantially linear olefin polymers also have a melt flow ratio, $I_{10}/I_2, \geqq 5.63$, and a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63.$$

Compositions comprising the substantially linear olefin polymer and at least one other natural or synthetic polymer are also within the scope of the invention.

Elastic substantially linear olefin polymers comprising ethylene homopolymers or an interpolymer of ethylene with at least one C_3–C_{20} α-olefin copolymers are especially preferred.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 graphically displays dynamic shear viscosity data for an elastic substantially linear olefin polymer of the present invention and for a comparative linear polymer made using single site catalyst technology.

DETAILED DESCRIPTION OF THE INVENTION

Other properties of the substantially linear polymers include:

a) a density from about 0.85 grams/cubic centimeter (g/cm^3) to about 0.97 g/cm^3, and

b) a melt index, I_2, from about 0.01 grams/10 minutes to about 1000 gram/10 minutes.

Preferably the melt flow ratio, I_{10}/I_2, is from about 7 to about 20.

The molecular weight distribution (M_w/M_n) is preferably less than about 5, especially from about 1.5 to about 2.5, and most preferably from about 1.7 to about 2.3.

Throughout this disclosure, "melt index" or "I_2" is measured in accordance with ASTM D-1238 (190° C./2.16 kg); "I_{10}" is measured in accordance with ASTM D-1238 (190° C./10 kg).

The melt tension of these new polymers is also surprisingly good, e.g., as high as about 2 grams or more, especially for polymers which have a very narrow molecular weight distribution (i.e., M_2/M_n from about 1.5 to about 2.5).

The substantially linear polymers of the present invention can be homopolymers of C_2–C_{20} α-olefins, such as ethylene, propylene, 4-methyl-1-pentene, etc., or they can be interpolymers of ethylene with at least one C_3–C_2α-olefin and/or C_2–C_{20} acetylenically unsaturated monomer and/or C_4–C_{18} diolefins. The substantially linear polymers of the present invention can also be interpolymers of ethylene with at least one of the above C_3–C_{20} α-olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers.

Monomers usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, polyenes, carbon monoxide, etc. Preferred monomers include the C_2–C_{10} α-olefins especially ethylene, 1-propene, isobutylene, 1-butene, 1 hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (e.g., cyclo pentene, cyclo-hexene and cyclo-octene).

Other unsaturated monomers usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, conjugated or nonconjugated dienes, polyenes, etc. Preferred monomers include the C_2–C_{10} α-olefins especially ethylene, 1-propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (e.g., cyclopentene, cyclohexene and cyclooctene).

The term "substantially linear" polymers means that the polymer backbone is substituted with about 0.01 long chain branches/1000 carbons to about 3 long chain branches/1000 carbons, more preferably from about 0.01 long chain branches/1000 carbons to about 1 long chain branches/1000 carbons, and especially from about 0.05 long chain branches/1000 carbons to about 1 long chain branches/1000 carbons.

The term "linear olefin polymers" means that the olefin polymer does not have long chain branching. That is, the linear olefin polymer has an absence of long chain branching, as for example the traditional linear low density polyethylene polymers or linear high density polyethylene polymers made using Ziegler polymerization processes (e.g., U.S. Pat. No. 4,076,698 or U.S. Pat. No. 3,645,992, the disclosures of which are incorporated herein by reference). The term "linear olefin polymers" does not refer to high pressure branched polyethylene, ethylene/vinyl acetate copolymers, or ethylene/vinyl alcohol copolymers which are known to those skilled in the art to have numerous long chain branches.

Long chain branching is defined herein as a chain length of at least about 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy. The long chain branch can be as long as about the same length as the length of the polymer back-bone.

Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method of Randall (*Rev. Macromol. Chem. Phys.*, C_{29} (2&3), p. 285–297), the disclosure of which is incorporated herein by reference.

"Melt tension" is measured by a specially designed pulley transducer in conjunction with the melt indexer. Melt tension is the load that the extrudate or filament exerts while passing over the pulley at the standard speed of 30 rpm. The melt tension measurement is similar to the "Melt Tension Tester" made by Toyoseiki and is described by John Dealy in "Rheometers for Molten Plastics", published by Van Nostrand Reinhold Co. (1982) on page 250–251.

The SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, *Journal of Polymer Science. Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), or in U.S. Pat. No. 4,798,081, both disclosures of which are incorporated herein by reference. The SCBDI or CDBI for the new polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent.

A unique characteristic of the presently claimed polymers is a highly unexpected flow property where the I_{10}/I_2 value is essentially independent of polydispersity index (i.e. M_w/M_n). This is contrasted with conventional polyethylene resins having rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases.

The density of the ethylene or ethylene/α-olefin substantially linear olefin polymers in the present invention is measured in accordance with ASTM D-792 and is generally from about 0.85 g/cm^3 to about 0.97 g/cm^3, preferably from about 0.85 g/cm^3 to about 0.9 g/cm^3, and especially from about 0.85 g/cm^3 to about 0.88 g/cm^3.

The molecular weight of the ethylene or ethylene/α-olefin substantially linear olefin polymers in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190° C./2.16 kg (formally known as "Condition (E)" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The melt index

for the ethylene or ethylene/α-olefin substantially linear olefin polymers used herein is generally from about 0.01 grams/10 minutes (g/10 min) to about 1000 g/10 min, preferably from about 0.01 g/10 min to about 100 g/10 min, and especially from about 0.01 g/10 min to about 10 g/10 min.

Additives such as antioxidants (e.g., hindered phenolics (e.g., Irganox® 1010), phosphites (e.g., Irgafos® 168)), cling additives (e.g., PIB), antiblock additives, pigments, and the like can also be included in the polyethylene compositions, to the extent that they do not interfere with the enhanced properties discovered by Applicants.

The compositions comprising the substantially linear olefin polymers are formed by any convenient method, including dry blending the individual components and subsequently melt mixing, either directly in the extruder used to make the finished article (e.g., film), or by premelt mixing in a separate extruder. The polyethylene compositions may also be prepared by multiple reactor polymerization techniques. For example, one reactor may polymerize the constrained geometry catalyzed polyethylene and another reactor polymerize the heterogeneous catalyzed polyethylene, either in series or in parallel operation.

The improved melt elasticity and processibility of the substantially linear polymers according to the present invention result, it is believed, from their method of production. The polymers may be produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor, but can also be produced using multiple reactors (e.g., using a multiple reactor configuration as described in U.S. Pat. No. 3,914,342) at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties. According to one embodiment of the present process, the polymers are produced in a continuous process, as opposed to a batch process. Preferably, the polymerization temperature is from about 20° C. to about 250° C., using constrained geometry catalyst technology. If a narrow molecular weight distribution polymer (M_w/M_n of from about 1.5 to about 2.5) having a higher I_{10}/I_2 ratio (e.g. I_{10}/I_2 of about 7 or more, preferably at least about 8, especially at least about 9) is desired, the ethylene concentration in the reactor is preferably not more than about 8 percent by weight of the reactor contents, especially not more than about 4 percent by weight of the reactor contents. Preferably, the polymerization is performed in a solution polymerization process. Generally, manipulation of I_{10}/I_2 while holding M_w/M_n relatively low for producing the novel polymers described herein is a function of reactor temperature and/or ethylene concentration. Reduced ethylene concentration and higher temperature generally produces higher $I10/I_2$.

Molecular Weight Distribution Determination

The whole interpolymer product samples and the individual interpolymer samples are analyzed by gel permeation chromatography (GPC) on a Waters 150° C. high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10^3, 10^4, 10^5, and 10^6), operating at a system temperature of 140° C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliters/minute and the injection size is 200 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are 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 following equation:

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

In this equation, $a=0.4316$ and $b=1.0$. Weight average molecular weight, M_w, is calculated in the usual manner according to the following formula: $M_w = R\ w_i^* M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the i^{th} fraction eluting from the GPC column.

Processing Index Determination

The rheological processing index (PI) is measured by a gas extrusion rheometer (GER). The GER is described by M. Shida, R. N. Shroff and L. V. Cancio in Polym. Eng. Sci., Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97–99, the disclosures of both of which are incorporated herein by reference. The processing index is measured at a temperature of 190° C., at nitrogen pressure of 2500 psig using 0.0296 inch diameter, 20:1 L/D die having an entrance angle of 180°. The GER processing index is calculated in millipoise units from the following equation:

$$PI = 2.15\times10^6\ \text{dynes/cm}^2/(1000\times\text{shear rate}),$$

where: 2.15×10^6 dynes/cm^2 is the shear stress at 2500 psi, and the shear rate is the shear rate at the wall as represented by the following equation:

$$32\ Q'/(60\ \text{sec/min})(0.745)(\text{Diameter}\times2.54\ \text{cm/in})^3,$$

where:

Q′ is the extrusion rate (gms/min),

0.745 is the melt density of polyethylene (gm/cm^3), and

Diameter is the orifice diameter of the capillary (inches). The PI is the apparent viscosity of a material measured at apparent shear stress of 2.15×10^6 dyne/cm^2.

For the substantially linear olefin polymers disclosed herein, the PI is less than or equal to 70 percent of that of a comparative linear olefin polymer at about the same I_2 and M_w/M_n. An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in *Journal of Rheology*, 30(2), 337–357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40× magnification. The critical shear rate

at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

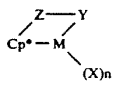
The Constrained Geometry Catalyst

Suitable constrained geometry catalysts for use herein preferably include constrained geometry catalysts as disclosed in U.S. application Ser. Nos.: 545,403, filed Jul. 3, 1990; Ser. No. 758,654, filed Sep. 12, 1991; Ser. No. 758,660, filed Sep. 12, 1991; and Ser. No. 720,041, filed Jun. 24, 1991, the teachings of all of which are incorporated herein by reference. The monocyclopentadienyl transition metal olefin polymerization catalysts taught in U.S. Pat. No. 5,026,798, the teachings of which are incorporated herein by reference, are also suitable for use in preparing the polymers of the present invention.

The foregoing catalysts may be further described as comprising a metal coordination complex comprising a metal of groups 3–10 or the Lanthanide series

of the Periodic Table of the Elements and a delocalized π-bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted π-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π-bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted x-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π-bonded moiety. The catalyst further comprises an activating cocatalyst.

Preferred catalyst complexes correspond to the formula:



wherein:

M is a metal of group 3–10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

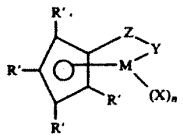
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

Y is an anionic or nonanionic ligand group bonded to Z and M comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system.

More preferably still, such complexes correspond to the formula:



wherein:

R' each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms;

X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, neutral Lewis base ligands and combinations thereof having up to 20 non-hydrogen atoms;

Y is —O—, —S—, —NR*—, —PR*—, or a neutral two electron donor ligand selected from the group consisting of OR*, SR*, NR^*_2 or PR^*_2;

M is as previously defined; and

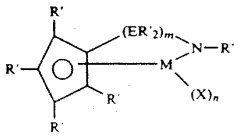
Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*{=}CR^*$, $CR^*_2SiR^*_2$, GeR^*_2, BR^*, BR^*_2; wherein

R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and n is 1 or 2.

It should be noted that whereas formula I and the following formulas indicate a cyclic structure for the catalysts, when Y is a neutral two electron donor ligand, the bond between M and Y is more accurately referred to as a coordinate-covalent bond. Also, it should be noted that the complex may exist as a dimer or higher oligomer.

Further preferably, at least one of R', Z, or R* is an electron donating moiety. Thus, highly preferably Y is a nitrogen or phosphorus containing group corresponding to the formula —N(R'')— or —P(R'')—, wherein R'' is C_{1-10} alkyl or aryl, i.e., an amido or phosphido group.

Most highly preferred complex compounds are amidosilane- or amidoalkanediyl- compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, aryl, aryloxy or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2.

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc. Specific compounds include: (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl) 1,2-ethanediyltitanium dichloride, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido)(tetramethyl-η^5 cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido)(tetramethyl-η^5-cyclopentadienyl)-methylenetitanium dichloro, (tert-butylamido)dibenzyl(tetramethyl-η^5-cyclopentadienyl) silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dichloride, (phenylphosphido)dimethyl(tetramethyl η^5-cyclopentadienyl)silanezirconium dibenzyl, (tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dimethyl, and the like.

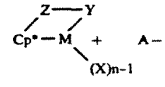
The complexes may be prepared by contacting a derivative of a metal, M, and a group I metal derivative or Grignard derivative of the cyclopentadienyl compound in a solvent and separating the salt byproduct. Suitable solvents for use in preparing the metal complexes are aliphatic or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane, heptane, tetrahydrofuran, diethyl ether, benzene, toluene, xylene, ethylbenzene, etc., or mixtures thereof.

In a preferred embodiment, the metal compound is MX_{n+1}, i.e., M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. The oxidation is accomplished merely by contacting the reactants utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "noninterfering oxidizing agent" is meant a compound having an oxidation potential sufficient to raise the metal oxidation state without interfering with the desired complex formation or subsequent polymerization processes. A particularly suitable noninterfering oxidizing agent is AgCl or an organic halide such as methylene chloride. The foregoing techniques are disclosed in U.S. Ser. Nos.: 545,403, filed Jul. 3, 1990 and Ser. No. 702,475, filed May 20, 1991, the teachings of both of which are incorporated herein by reference.

Additionally the complexes may be prepared according to the teachings of the copending application serial number 778,433 entitled: "Preparation of Metal Coordination Complex (I)", filed in the names of Peter Nickias and David Wilson, on Oct. 15, 1991 and the copending application Ser. No. 778,432 entitled: "Preparation of Metal Coordination Complex (II)", filed in the names of Peter Nickias and David Devore, on Oct. 15, 1991, the teachings of which are incorporated herein by reference thereto.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. So-called modified methyl aluminoxane (MMAO) is also suitable for use as a cocatalyst. One technique for preparing such modified aluminoxane is disclosed in U.S. Pat. No. 5,041,584, the teachings of which are incorporated herein by reference. Aluminoxanes can also be made as disclosed in U.S. Pat. Nos. 5,542,199; 4,544,762; 5,015,749; and 5,041,585, the entire specification of each of which is incorporated herein by reference. Preferred cocatalysts are inert, noncoordinating, boron compounds.

Ionic active catalyst species which can be used to polymerize the polymers described herein correspond to the formula:



wherein:

M is a metal of group 3–10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and 20 optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

A- is a noncoordinating, compatible anion.

One method of making the ionic catalyst species which can be utilized to make the polymers of the present invention involve combining:

a) at least one first component which is a mono(cyclopentadienyl) derivative of a metal of Group 3–10 or the Lanthanide Series of the Periodic Table of the Elements containing at least one substituent which will combine with the cation of a second component (described hereinafter) which first component is capable of forming a cation formally having a coordination number that is one less than its valence, and

b) at least one second component which is a salt of a Bronsted acid and a noncoordinating, compatible anion.

More particularly, the non-coordinating, compatible anion of the Bronsted acid salt may comprise a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and non-nucleophilic. The recitation "metalloid", as used herein, includes non metals such as boron, phosphorus and the like which exhibit semi-metallic characteristics.

Illustrative, but not limiting examples of monocyclopentadienyl metal components (first components)

which may be used in the preparation of cationic complexes are derivatives of titanium, zirconium, vanadium, hafnium, chromium, lanthanum, etc. Preferred components are titanium or zirconium compounds. Examples of suitable monocyclopentadienyl metal compounds are hydrocarbyl-substituted monocyclopentadienyl metal compounds such as (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dimethyl, (tertbutylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dibenzyl, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (ethylamido)(tetramethyl η^5-cyclopentadienyl)methylenetitanium dimethyl, (tertbutylamido)dibenzyl(tetramethyl-η^5-cyclopentadienyl) silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)-silanetitanium diphenyl, (phenylphosphido)dimethyl(-tetramethyl-η^5-cyclopentadienyl)silanezirconium dibenzyl, and the like.

Such components are readily prepared by combining the corresponding metal chloride with a dilithium salt of the substituted cyclopentadienyl group such as a cyclopentadienyl-alkanediyl, cyclopentadienyl—silane amide, or cyclopentadienyl—phosphide compound. The reaction is conducted in an inert liquid such as tetrahydrofuran, C_{5-10} alkanes, toluene, etc. utilizing conventional synthetic procedures. Additionally, the first components may be prepared by reaction of a group II derivative of the cyclopentadienyl compound in a solvent and separating the salt by-product. Magnesium derivatives of the cyclopentadienyl compounds are preferred. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. The resulting metal cyclopentadienyl halide complexes may be alkylated using a variety of techniques. Generally, the metal cyclopentadienyl alkyl or aryl complexes may be prepared by alkylation of the metal cyclopentadienyl halide complexes with alkyl or aryl derivatives of group I or group II metals. Preferred alkylating agents are alkyl lithium and Grignard derivatives using conventional synthetic techniques. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. A preferred solvent is a mixture of toluene and tetrahydrofuran.

Compounds useful as a second component in the preparation of the ionic catalysts useful in this invention will comprise a cation, which is a Bronsted acid capable of donating a proton, and a compatible noncoordinating anion. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 3–10 or Lanthanide Series cation) which is formed when the two components are combined and sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Suitable metals, then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

Highly preferably, the second component useful in the preparation of the catalysts of this invention may be represented by the following general formula:

$$(L-H)^+ [A]^-$$

wherein:

L is a neutral Lewis base;

$(L-H)^+$ is a Bronsted acid; and

$[A]^-$ is a compatible, noncoordinating anion.

More preferably $[A]^-$ corresponds to the formula:

$$[M'Q_q]^-$$

wherein:

M' is a metal or metalloid selected from Groups 5–15 of the Periodic Table of the Elements; and

Q independently each occurrence is selected from the Group consisting of hydride, dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide and

q is one more than the valence of M'.

Second components comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

$$[L-H]^+ [BQ_4]^-$$

wherein:

L is a neutral Lewis base;

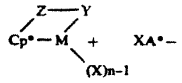
$[L-H]^+$ is a Bronsted acid;

B is boron in a valence state of 3; and

Q is as previously defined.

Illustrative, but not limiting, examples of boron compounds which may be used as a second component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tris(n-butyl)ammonium tetraphenylborate, trimethylammonium tetrakis(p-tolyl)-borate, tributylammonium tetrakis(pentafluorophenyl)-borate, tripropylammonium tetrakis(2,4-dimethylphenyl)borate, tributylammonium tetrakis(3,5-dimethylphenyl)borate, triethylammonium tetrakis(3,5-ditrifluoromethylphenyl)borate and the like. Also suitable are N,N-dialkyl anilinium salts such as N,N-dimethylaniliniumtetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-2,4,6-pentamethylanilinium tetraphenylborate and the like; dialkylammonium salts such as di-(i-propyl)ammonium tetrakis(pentafluorophenyl)-borate, dicyclohexylammonium tetraphenylborate and the like; and triaryl phosphonium salts such as triphenylphosphonium tetraphenylborate, tri(methylphenyl)phosphonium tetrakispentafluorophenylborate, tri(dimethylphenyl)phosphonium tetraphenylborate and the like.

Preferred ionic catalysts are those having a limiting charge separated structure corresponding to the formula:



wherein:

M is a metal of group 3–10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

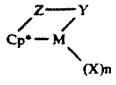
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

XA^*- is $-XB(C_6F_5)_3$.

This class of cationic complexes may be conveniently prepared by contacting a metal compound corresponding to the formula:

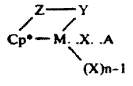


wherein:

Cp*. M, and n are as previously defined, with tris(pentafluorophenyl)borane cocatalyst under conditions to cause abstraction of X and formation of the anion $-XB(C_6F_5)_3$.

Preferably X in the foregoing ionic catalyst is C_1C_{10} hydrocarbyl, most preferably methyl.

The preceding formula is referred to as the limiting, charge separated structure. However, it is to be understood that, particularly in solid form, the catalyst may not be fully charge separated. That is, the X group may retain a partial covalent bond to the metal atom, M. Thus, the catalysts may be alternately depicted as possessing the formula:



The catalysts are preferably prepared by contacting the derivative of a Group 4 or Lanthanide metal with the tris(pentafluorophenyl)borane in an inert diluent such as an organic liquid. Tris(pentafluorphenyl)borane is a commonly available Lewis acid that may be readily prepared according to known techniques. The compound is disclosed in Marks, et al. *J. Am. Chem. Soc.* 1991, 113, 3623–3625 for use in alkyl abstraction of zirconocenes.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

It is believed that in the constrained geometry catalysts used herein the metal atom is forced to greater exposure of the active metal site because one or more substituents on the single cyclopentadienyl or substituted metal is both bonded to an adjacent covalent moiety and held in association with the cyclopentadienyl group through an η^5 or other π-bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is, the metal may be symmetrically or unsymmetrically π-bound to the cyclopentadienyl or substituted cyclopentadienyl group.

The geometry of the active metal site is further defined as follows. The centroid of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The angle, Θ, formed at the metal center between the centroid of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, Θ, is less than in a similar, comparative complex differing only in the fact that the constrain inducing substituent is replaced by hydrogen, have constrained geometry for purposes of the present invention. Preferably one or more of the above angles, Θ, decrease by at least 5 percent, more preferably 7.5 percent, compared to the comparative complex. Highly preferably, the average value of all bond angles, Θis also less than in the comparative complex.

Preferably, monocyclopentadienyl metal coordination complexes of group 4 or lanthanide metals according to the present invention have constrained geometry such that the smallest angle, Θ between the centroid of the Cp* group and the Y substituent, is less than 115°, more preferably less than 110°, most preferably less than 105°, and especially less than 100°.

Other compounds which are useful in the catalyst compositions of this invention, especially compounds containing other Group 4 or Lanthanide metals, will, of course, be apparent to those skilled in the art.

Polymerization

The polymerization conditions for manufacturing the polymers of the present invention are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Slurry and gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Multiple reactor polymerization processes are also useful in the present invention, such as those disclosed in U.S. Pat. No. 3,914,342, incorporated herein by reference. The multiple reactors can be operated in series or in parallel, with at least one constrained geometry catalyst employed in at least one of the reactors.

In general, the continuous polymerization according to the present invention may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0° to 250° C. and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspen-

sion, solution, slurry, gas phase or other process conditions may be employed if desired. A support may be employed but preferably the catalysts are used in a homogeneous (i.e., soluble) manner. It will, of course, be appreciated that the active catalyst system, especially nonionic catalysts, form in situ if the catalyst and the cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

The polymerization conditions for manufacturing the polymers of the present invention are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Fabricated articles made from the novel olefin polymers may be prepared using all of the conventional polyolefin processing techniques. Useful articles include films (e.g., cast, blown and extrusion coated), fibers (e.g., staple fibers (including use of a novel olefin polymer disclosed herein as at least one component comprising at least a portion of the fiber's surface), spunbound fibers or melt blown fibers (using, e.g., systems as disclosed in U.S. Pat. No. 4,340,563, U.S. Pat. No. 4,663,220, U.S. Pat. No. 4,668,566, or U.S. Pat. No. 4,322,027, all of which are incorporated herein by reference), and gel spun fibers (e.g., the system disclosed in U.S. Pat. No. 4,413,110, incorporated herein by reference)), both woven and nonwoven fabrics (e.g., spunlaced fabrics disclosed in U.S. Pat. No. 3,485,706, incorporated herein by reference) or structures made from such fibers (including, e.g., blends of these fibers with other fibers, e.g., PET or cotton) and molded articles (e.g., made using an injection molding process, a blow molding process or a rotomolding process). The new polymers described herein are also useful for wire and cable coating operations, impact modification, especially at low temperatures, of thermoplastic olefins (e.g., polypropylene), as well as in sheet extrusion for vacuum forming operations.

Useful compositions are also suitably prepared comprising the substantially linear polymers of the present invention and at least one other natural or synthetic polymer. Preferred other polymers include thermoplastics such as styrene-butadiene block copolymers, polystyrene (including high impact polystyrene), ethylene vinyl alcohol copolymers, ethylene acrylic acid copolymers, other olefin copolymers (especially polyethylene copolymers) and homopolymers (e.g., those made using conventional heterogeneous catalysts). Examples include polymers made by the process of U.S. Pat. No. 4,076,698, incorporated herein by reference, other linear or substantially linear polymers of the present invention, and mixtures thereof. Other substantially linear polymers of the present invention and conventional HDPE and/or LLDPE are preferred for use in the thermoplastic compositions.

Compositions comprising the olefin polymers can also be formed into fabricated articles such as those previously mentioned using conventional polyolefin processing techniques which are well known to those skilled in the art of polyolefin processing.

All procedures were performed under an inert atmosphere or nitrogen or argon. Solvent choices were often optional, for example, in most cases either pentane or 30-60 petroleum ether can be interchanged. Amines, silanes, lithium reagents, and Grignard reagents were purchased from Aldrich Chemical Company. Published methods for preparing tetramethylcyclopentadiene ($C_5Me_4H_2$) and lithium tetramethylcyclopentadienide ($Li(C_5Me_4H)$) include C. M. Fendrick et al. *Organometallics*, 3, 819 (1984). Lithiated substituted cyclopentadienyl compounds may be typically prepared from the corresponding cyclopentadiene and a lithium reagent such as n-butyl lithium. Titanium trichloride (TiC_{13}) was purchased from Aldrich Chemical Company. The tetrahydrofuran adduct of titanium trichloride, $TiC_{13}(THF)_3$, was prepared by refluxing TiC_{13} in THF overnight, cooling, and isolating the blue solid product, according to the procedure of L. E. Manzer, *Inorg. Syn.*, 21, 135 (1982).

EXAMPLES

The polymer products of Examples 1 and 3 are produced in a continuous solution polymerization process using a continuously stirred reactor, as described in copending application serial number 07/776,130, filed Oct. 15, 1991. The metal complex $[C_5Me_4(SiMe_2N\text{-}^tBu)]TiMe_2$ is prepared as described in copending application Ser. No. 07/776,130 and the cocatalysts used are tris(pentafluorophenyl) borane (*B*:Ti ratio of 2:1) and MMAO (Al:Ti ratio of 4:1). For Example 1 the ethylene concentration in the reactor is about 1.10% and for Example 3 the ethylene concentration in the reactor is about 1.02% (percentages based on the weight of the reactor contents). For each Example, the reactor is run without hydrogen.

Additives (e.g., antioxidants, pigments, etc.) can be incorporated into the interpolymer products either during the pelletization step or after manufacture, with a subsequent re-extrusion. Examples 1 and 3 are each stabilized with 1250 ppm Calcium Stearate, 200 ppm Irganox 1010, and 1600 ppm Irgafos 168. Irgafos TM 168 is a phosphite stabilizer and Irganox TM 1010 is a hindered polyphenol stabilizer (e.g., tetrakis [methylene 3-(3,5-ditert.butyl-4-hydroxyphenylpropionate)]methane. Both are trademarks of and made by Ciba-Geigy Corporation.

Example 1 and Comparative Example 2

Example 1 is an ethylene/1 octene elastic substantially linear olefin polymer produced as described herein.

Comparative Example 2 is an ethylene/1-butene copolymer containing butylated hydroxy toluene (BHT) and Irganox TM 1076 made by Exxon Chemical and trademarked Exact TM . Table 1 summarizes physical properties and rheological performance of these two polymers:

TABLE 1

Property	Example 1	Comparative Example 2
I_2 (g/10 minutes)	3.3	3.58
Density (g/cm^3)	0.870	0.878
I_{10}/I_2	7.61	5.8
M_w/M_n	1.97	1.95
PI (kPoise)	3.2	8.4

TABLE 1-continued

Property	Example 1	Comparative Example 2
Elastic Modulus @ 0.1 rad/sec (dynes/cm^2)	87.7	8.3
OSMF*, critical shear rate (sec^{-1})	660	250

*Onset of surface melt fracture

Even though Example 1 and Comparative Example 2 have very similar molecular weight distributions (M_w/M_n), I_2 and density, Example 1 has a much lower processing index (PI) (38% of the PI of Comparative Example 2), a much higher onset of surface melt fracture (264% increase in OSMF) and an elastic modulus an order of magnitude higher than Comparative Example 2, demonstrating that Example 1 has much better processability and higher melt elasticity than Comparative Example 2.

Elastic modulus is indicative of a polymer's melt stability, e.g., more stable bubbles when making blown film and less neck-in. Resultant physical properties of the finished film are also higher.

Onset of surface melt fracture is easily identified by visually observing the surface extrudate and noting when the extrudate starts losing gloss and small surface roughness is detected by using 40× magnification.

Dynamic shear viscosity of the polymers is also used to show differences between the polymers and measures viscosity change versus shear rate. A Rheometrics Mechanical Spectrometer (Model RMS 800) is used to measure viscosity as a function of shear rate. The RMS 800 is used at 190° C. at 15% strain and a frequency sweep (i.e., from 0.1–100 rad/sec) under a nitrogen purge. The parallel plates are positioned such that they have a gap of about 1.5–2 mm. Data for Example 1 and Comparative Example 2 are listed in Table 2 and graphically displayed in FIG. 1.

TABLE 2

Shear Rate (rad/sec)	Dynamic Viscosity (poise) for Example 1	Dynamic Viscosity (poise) for Comparative Example 2
0.1	28290	18990
0.1585	28070	18870
0.2512	27630	18950
0.3981	27140	18870
0.631	26450	18840
1	25560	18800
1.585	24440	18690
2.512	23140	18540
3.981	21700	18310
6.31	20170	17960
10	18530	17440
15.85	16790	16660
25.12	14960	15620
39.81	13070	14310
63.1	11180	12750
100	9280	10960

Surprisingly, Example 1 shows a shear thinning behaviour, even though Example 1 has a narrow molecular weight distribution. In contrast, Comparative Example 2 shows the expected behaviour of a narrow molecular weight distribution polymer, with a flatter viscosity/shear rate curve.

Thus, elastic substantially linear olefin polymers made in accordance with the present invention (e.g. Example 1) have lower melt viscosity than a typical narrow molecular weight distribution linear copolymer made by single site catalyst technology at the melt processing shear rate region of commercial interest. In addition, the novel elastic substantially linear olefin polymers have a higher low shear/zero shear viscosity than the Comparative linear polymer, thus demonstrating that the copolymers of the invention have higher "green strength" which is useful for forming and maintaining blended compositions such as those used in the wire and cable coating industry, where the compounded materials must maintain their integrity at low or zero shear without segregating the components.

Example 3 and Comparative Example 4

Example 3 is an ethylene/1-octene elastic substantially linear olefin polymer produced in a continuous solution polymerization process as described herein.

Comparative Example 4 is an ethylene/1-propene copolymer made by Mitsui PetroChemical Corporation and trademarked Tafmer TM P-0480. Table 3 summarizes physical properties and rheological performance of these two polymers:

TABLE 3

Property	Example 3	Comparative Example 4
I_2 (g/10 minutes)	1.01	1.1
Density (g/cm^3)	0.870	0.870
I_{10}/I_2	7.62	6.06
M_w/M_n	1.98	1.90
PI (kPoise)	7.9	27.4
Elastic Modulus @ 0.1 rad/sec (dynes/cm^2)	964	567.7
OSMF*, critical shear rate (sec^{-1})	781	105

*Onset of surface melt fracture

Even though Example 3 and Comparative Example 4 have similarly narrow molecular weight distributions (M_w/M_n), I_2, and density, Example 3 has a PI which is 28% of that of Comparative Example 4, a 743% increase in onset of surface melt fracture and a higher elastic modulus than Comparative Example 4, demonstrating that Example 3 has much better processability than Comparative Example 4. Onset of surface melt fracture is easily identified by visually observing the surface extrudate and noting when the extrudate starts losing gloss and small surface roughness is detected by using 40× magnification.

We claim:

1. A substantially linear olefin polymer characterized as having:

a) a melt flow ratio, $I_{10}/I_2, \geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n. and wherein the olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

2. The substantially linear olefin polymer of claim 1 wherein the M_w/M_n is less than about 3.5.

3. The substantially linear olefin polymer of claim 1 wherein the M_w/M_n is from about 1.5 to about 2.5.

4. The substantially linear olefin polymer of claim 3 wherein the I_{10}/I_2 is at least about 8.

5. The substantially linear olefin polymer of claim 3 wherein the I_{10}/I_2 is at least about 9.

6. The substantially linear olefin polymer of claim 1 wherein the polymer is a substantially linear ethylene polymer having from about 0.01 to about 3 long chain branches/1000 carbons along the polymer backbone.

7. The substantially linear olefin polymer of claim 4 having at least about 0.05 long chain branches/1000 carbons along the polymer backbone.

8. The substantially linear olefin polymer of claim 4 having at least about 0.3 long chain branches/1000 carbons along the polymer backbone.

9. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 1-octene.

10. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 1-hexene.

11. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 1-butene.

12. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 4-methyl-1-pentene.

13. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 1-octene.

14. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 1-hexene.

15. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 1-butene.

16. The substantially linear olefin polymer of claim 1, wherein the polymer is a copolymer of ethylene and 4-methyl-1-pentene.

17. A composition comprising a substantially linear olefin polymer, wherein the polymer is characterized as having:

a) a melt flow ratio, $I_{10}/I_2, \geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n, and wherein the olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin and (b) at least one other natural or synthetic polymer.

18. The composition of claim 17 wherein the substantially linear olefin polymer has a I_{10}/I_2 up to about 20.

19. The composition of claim 17 wherein the substantially linear olefin polymer has a M_w/M_n less than about 3.5.

20. The composition of claim 17 wherein the substantially linear olefin polymer has a M_w/M_n from about 1.5 to about 2.5.

21. The composition of claim 17 wherein the synthetic polymer is a conventional olefin polymer.

22. The composition of claim 17, wherein the substantially linear olefin polymer is a copolymer of ethylene and 1-octene.

23. The composition of claim 17, wherein the substantially linear olefin polymer is a copolymer of ethylene and 1-hexene.

24. The composition of claim 17, wherein the substantially linear olefin polymer is a copolymer of ethylene and 1-butene.

25. The composition of claim 17, wherein the substantially linear olefin polymer is a copolymer of ethylene and 4-methyl-1-pentene.

26. A substantially linear olefin polymer characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin and having:

a) a melt flow ratio, $I_{10}/I_2, \geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a processing index (PI) less than or equal to about 70% of the PI of a comparative linear olefin polymer at about the same I_2 and M_w/M_n.

27. The substantially linear olefin polymer of claim 1, wherein the polymer is in pelletized form.

28. The pelletized substantially linear olefin polymer of claim 27, wherein the density of the polymer is from about 0.85 g/cm^3 to about 0.9 g/cm^3.

29. The pelletized substantially linear olefin polymer of claim 27, wherein the density of the polymer is from about 0.85 g/cm^3 to about 0.88 g/cm^3.

30. The substantially linear olefin polymer of claim 1, wherein the polymer is in pelletized form.

31. The pelletized substantially linear olefin polymer of claim 30, wherein the density of the polymer is from about 0.85 g/cm^3 to about 0.9 g/cm^3.

32. The pelletized substantially linear olefin polymer of claim 30, wherein the density of the polymer is from about 0.85 g/cm^3 to about 0.88 g/cm^3.

33. The substantially linear olefin polymer of claim 26, wherein the polymer is in pelletized form.

34. The pelletized substantially linear olefin polymer of claim 33, wherein the density of the polymer is from about 0.85 g/cm^3 to about 0.9 g/cm^3.

35. The pelletized substantially linear olefin polymer of claim 33, wherein the density of the polymer is from about 0.85 g/cm^3 to about 0.88 g/cm^3.

36. A film layer comprising a substantially linear olefin polymer, wherein the substantially linear olefin polymer is characterized as having:

a) a melt flow ratio, $I_{10}/I_2, \geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a critical shear rate at onset of surface melt fracture at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n, and wherein the olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

37. A film layer composition comprising a substantially linear olefin polymer, wherein the substantially linear olefin polymer is characterized as having:

a) a melt flow ratio, $I_{10}/I_2, \geqq 5.63$,

b) a molecular weight distribution, M_w/M_n, of from 1.5 to 2.5, and

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer at about the same I_2 and M_w/M_n, and wherein the olefin polymer is further characterized as a copolymer of ethylene with a C_3–C_{20} alpha-olefin.

* * * * *

US005374700A

United States Patent [19]

Tsutsui et al.

[11] Patent Number: 5,374,700

[45] Date of Patent: Dec. 20, 1994

[54] ETHYLENE COPOLYMER

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[73] Assignee: Mitsui Petrochemical Industries, Ltd., Tokyo, Japan

[21] Appl. No.: 686,599

[22] Filed: Apr. 17, 1991

[30] Foreign Application Priority Data

Apr. 18, 1990 [JP] Japan 2-102160
May 14, 1990 [JP] Japan 2-123858
Aug. 8, 1990 [JP] Japan 2-211334

[51] Int. Cl.[5] C08F 210/16; C08F 4/602

[52] U.S. Cl. 526/348.3; 526/128; 526/129; 526/160; 526/348; 526/348.2; 526/348.5; 526/348.6; 526/904

[58] Field of Search 526/160, 348, 348.5, 526/348.6, 348.2, 348.3, 904, 128

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Primary Examiner—Fred Teskin
Attorney, Agent, or Firm—Sherman and Shalloway

[57] ABSTRACT

The present invention provides an ethylene copolymer comprising constituent units (a) derived from ethylene and constituent units (b) derived from an α-olefin having 3 to 20 carbon atoms, the ethylene copolymer being characterized in that

(A) the ethylene copolymer has a density (d) of 0.86 to 0.95 g/cm^3;

(B) the ethylene copolymer has a MFR of 0.001 to 50 g/10 min as measured at a temperature of 190° C. and a load of 2.16 kg;

(C) the melt tension (MT) and MFR of the ethylene copolymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6; \text{ and}$$

(D) the temperature (T) at which the exothermic curve of the ethylene copolymer measured by a differential scanning calorimeter (DSC) shows the highest peak and the density (d) satisfy the relation

$$T < 400d - 250.$$

2 Claims, 3 Drawing Sheets

FIG. 1

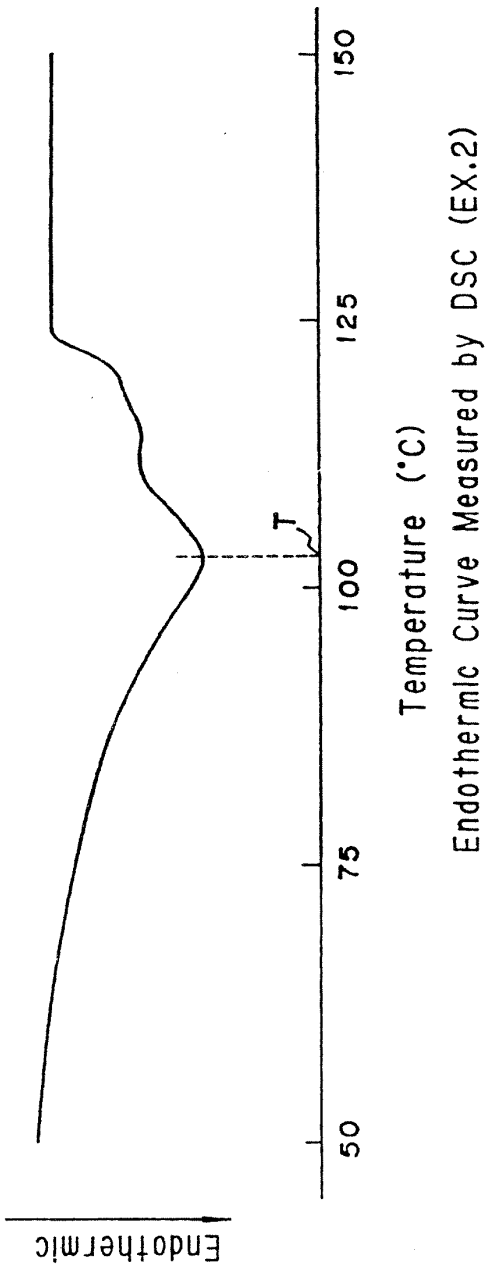

Endothermic
50
75
100
125
150
T
Temperature (°C)
Endothermic Curve Measured by DSC (EX.2)

FIG. 2

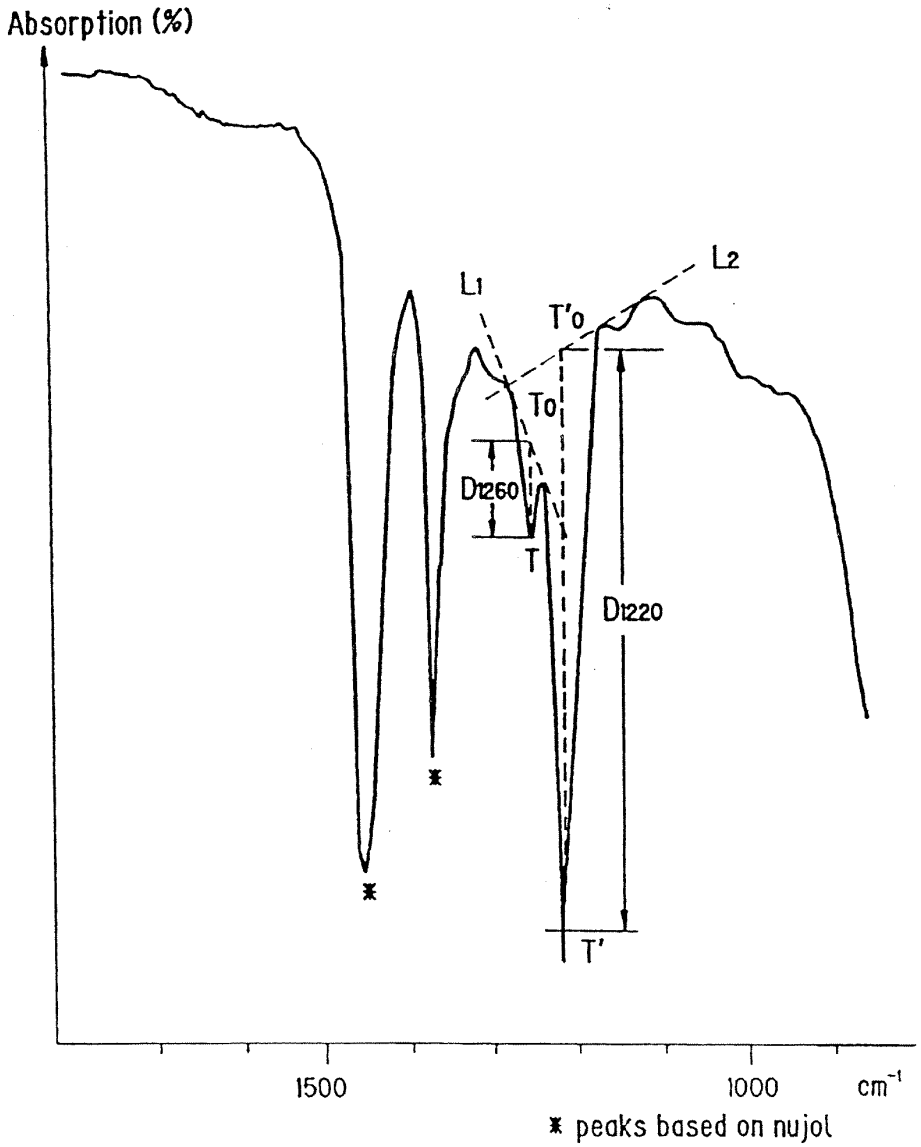
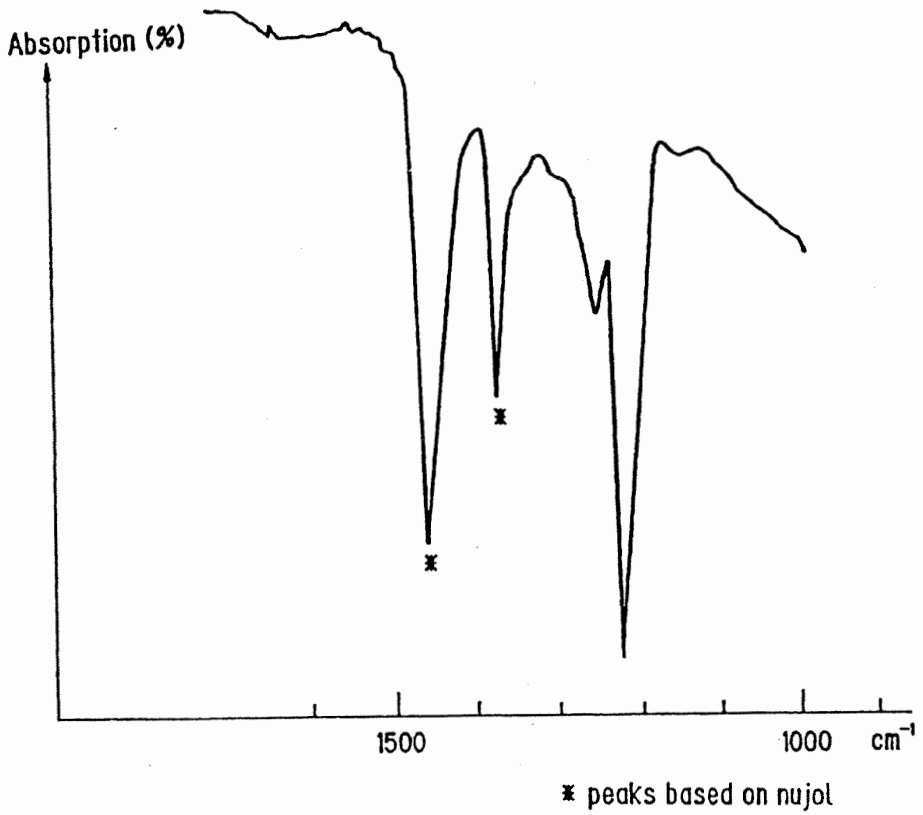

Absorption (%)
L1
L2
T'o
To
D1260
T
D1220
T'
1500
1000
cm⁻¹
* peaks based on nujol

FIG. 3



ETHYLENE COPOLYMER

FIELD OF THE INVENTION

The present invention relates to a novel ethylene copolymer, more particularly to a novel ethylene copolymer having a narrow composition distribution and an excellent melt tension compared with known ethylene copolymers.

Furthermore, the present invention relates to a process for the preparation of an olefin polymer, especially an ethylene polymer, more particularly to a process for the preparation of an ethylene polymer being excellent in melt tension, and, in the case of a copolymer, having a narrow composition distribution.

Still furthermore, the present invention relates to a solid catalyst for olefin polymerization and a process for olefin polymerization using the catalyst, more particularly to a solid catalyst for olefin polymerization applicable to process for suspension polymerization and a process for gas phase polymerization, capable of producing, with high polymerization activities, a sphere olefin polymer excellent in particle properties when applied to these polymerization processes with use of an organoaluminum oxy-compound in a decreased amount, and excellent in melt tension, and a process for olefin polymerization using the catalyst.

BACKGROUND OF THE INVENTION

Ethylene copolymers have heretofore been molded by various molding methods, and used in many fields. The requirement for the characteristics of the ethylene copolymers differ depending on the molding methods ant uses. For example, when an inflation film is molded at a high speed, it is necessary to select an ethylene copolymer having a high melt tension compared with its molecular weight in order to stably conduct high speed molding without fluctuation or tearing of bubbles. An ethylene copolymer is required to have similar characteristics in order to prevent sag or tearing in blow molding, or to suppress width shortage to the minimum range in T-die molding.

A high-pressure low density polyethylene has a high meat tension compared with an ethylene copolymer prepared with a Ziegler type catalyst, and is used as a material for films and hollow containers. The high-pressure low density polyethylene as described above has low mechanical strength such as tensile strength, tear strength and impact strength, and in addition it has also low heat resistance, low stress cracking resistance, etc.

On the other hand, Japanese Patent L-O-P Nos. 90810/1981 and 106806/1985 propose a method for improving the melt tension and blow ratio (die/swell ratio) of ethylene polymers obtained by using Ziegler type catalysts, especially a titanium type catalyst.

The ethylene polymers obtained by using a titanium catalyst, however, especially the low density ethylene polymers generally have problems such as their broad composition distribution and stickiness of their molded articles such as films.

Accordingly, the advent of ethylene polymers having an excellent melt tension and a narrow composition distribution will industrially be of great value.

There has recently been developed a new Ziegler type catalyst for olefin polymerization comprising a zirconium compound and an aluminoxane, said catalyst being capable of producing ethylene/α-olefin copolymers with high polymerization activities. There has also

been proposed a process for the preparation of ethylene/α-olefin copolymers using such a new type catalyst.

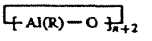
For example, Japanese Patent L-O-P No. 19309/1983 discloses a process for polymerizing ethylene with one or at least two C_3–C_{12} α-olefins at a temperature of −50° to 200° C., in the presence of a catalyst composed of a transition metal compound represented by the formula

$$(\text{cyclopentadienyl})_2\text{Me R Hal}$$

wherein R is cyclopentadienyl, C_1–C_6 alkyl or halogen, Me is a transition metal and Hal is halogen, and a linear aluminoxane represented by the formula

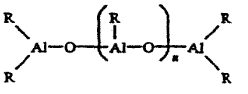
$$Al_2OR_4[Al(R)—O]_n$$

wherein R is methyl or ethyl, and n is a number of 4 to 20, or a cyclic aluminoxane represented by the formula

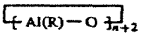


wherein R and n are as defined above.

Japanese Patent L-O-P No. 19309/1983 discloses an invention relating to processes for preparing a linear aluminoxane represented by the formula

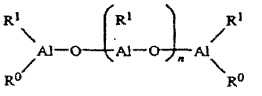


wherein n is a number of 2 to 40, and R is C_1–C_8 alkyl, and a cyclic aluminoxane represented by the formula



wherein n and R are as defined above. The same Patent Publication also discloses a process for the polymerization of olefin using a catalyst prepared by mixing, for example, methylaluminoxane prepared by the above-mentioned process and a bis(cyclopentadienyl) compound of titanium or zirconium.

Japanese Patent L-O-P No. 35005/1985 discloses a process for preparing an olefin polymerization catalyst, wherein the process comprises reacting an aluminoxane represented by the formula

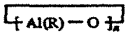


wherein R^1 is C_1–C_{10} alkyl, and R^O is R^1 or R^O represents —O— by linkage, with a magnesium compound at first, then chlorinating the reaction product, and treating with a compound of Ti, V, Zr or Cr.

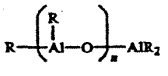
Japanese Patent L-O-P No. 35006/1985 discloses a catalyst composed of mono- di- or tricyclopentadienyl-transition metals (a) (transition metals being at least two different metals) or their derivatives and an alumoxane

(aluminoxane) in combination. Example 1 of this Patent publication discloses that ethylene and propylene are polymerized to form a polyethylene in the presence of a catalyst composed of bis(pentamethylcyclopentadienyl)zirconiumdimethyl and an aluminoxane. In Example 2 of this Patent publication, ethylene and propylene are polymerized to form a polymer blend of a polyethylene and an ethylene/propylene copolymer in the presence of a catalyst composed of bis(pentamethylcyclopentadienyl)zirconiumdichloride, bis(methylcyclopentadienyl)zirconium dichloride and an alumoxane.

Japanese Patent L-O-P No. 35007/1985 discloses a process wherein ethylene alone is polymerized, or ethylene and an α-olefin of not less than 3 carbon atoms are copolymerized in the presence of metallocene, and a cyclic aluminoxane represented by the formula



wherein R is an alkyl group of 1 to 5 carbon atoms, and n is an integer of 1 to about 20, or a linear aluminoxane represented by the formula



wherein R and n are as defined above.

Japanese Patent L-O-P No. 35008/1985 discloses a process for the preparation of a polyethylene or a copolymer of ethylene and a C_3–C_{10} α-olefin, wherein a catalyst system comprising not less than two types of metallocene and an alumoxane is used.

Though the catalysts formed from a transition metal compound and an aluminoxane proposed by the prior art are excellent in polymerization activities, especially ethylene polymerization activities compared with those catalysts having been known prior to the appearance of these catalysts and formed from a transition metal compound and an organolauminum compound, most of the catalysts are soluble in the reaction system, and in most cases the processes for the preparation are limited to a solution polymerization system. In addition, the catalysts have such a problem that the productivity of a polymer is lowered due to a marked increase in the viscosity of the polymer-containing reaction solution when the manufacture of a polymer having a high molecular weight is tried, that the polymer obtained by after-treatment of polymerization has a low bulk specific gravity, and that the preparation of a sphere polymer having excellent particle properties is difficult.

On the other hand, polymerization of olefin has been tried in a suspension polymerization system or a gas phase polymerization system by using catalysts in which at least one of the transition metal compound component and the aluminoxane component described above is supported on a porous inorganic oxide carrier such as silica, alumina and silica-alumina.

For example, Japanese Patent L-O-P Nos. 35006/1985, 35007/1985 and 35008/1985 described above disclose that there can be used catalysts in which a transition metal compound and an aluminoxane are supported on silica, alumina, silica-alumina, etc.

Furthermore, Japanese Patent L-O-P Nos. 106808/1985 and 106809/1985 disclose a process for the preparation of a composition composed of an ethylene polymer and a filler, which process comprises polymerizing ethylene or copolymerizing ethylene and α-olefin in the presence of a product prepared by contacting a highly activated catalyst component comprising a hydrocarbon-soluble titanium compound and/or a zirconium compound with a filler, an organoaluminum compound and a filler having an affinity for polyolefin.

Japanese Patent L-O-P No. 31404/1986 discloses a process for polymerizing ethylene or copolymerizing ethylene and an α-olefin in the presence of a catalyst mixture composed of a transition metal compound and a product obtained by the reaction of trialkylaluminum and water in the presence of silicon dioxide or aluminum oxide.

Furthermore, Japanese Patent L-O-P No. 276805/1986 discloses that olefin is polymerized in the presence of a catalyst composed of a zirconium compound and a reaction mixture obtained by reacting an aluminoxane with trialkylaluminum at first, and further by reacting the resultant reaction mixture with such an inorganic oxide having a hydroxide group on the surface as silica.

Still furthermore, Japanese Patent L-O-P Nos. 108610/1986 and 296008/1986 discloses a process for polymerizing olefin in the presence of a catalyst in which a transition metal compound such as metallocene and an aluminoxane are supported on a carrier such as an inorganic oxide.

However, during the polymerization or copolymerization of olefin in a suspension or gas phase by using such a solid catalyst component supported on a carrier as described in the above-mentioned Patent publns., the catalyst component considerably lowers the polymerization activities compared with the above-described solution polymerization, and the resulting polymers do not have a satisfactory bulk density.

OBJECT OF THE INVENTION

The present invention is intended to solve such problems associated with the prior art technique as described above, and an object of the invention is to provide an ethylene copolymer being excellent in melt tension and having a narrow composition distribution.

Another object of the present invention is to provide a process for the preparation of ethylene polymers being excellent in melt tension, and, in the case of a copolymer, having a narrow composition distribution.

A still further object of the invention is to provide solid catalysts for olefin polymerization capable of manufacturing with high activities sphere olefin polymers excellent in particle properties and melt tension even when they are applied to suspension polymerization and gas phase polymerization with an organoaluminum oxy-compound used not in a large quantity, and to carry out olefin polymerization by using such catalysts having good properties.

SUMMARY OF THE INVENTION.

The ethylene copolymer according to the present invention is an ethylene copolymer comprising constituent units (a) derived from ethylene and constituent units (b) derived from an (α-olefin having 3 to 20 carbon atoms, and is characterized in that:

(A) the ethylene copolymer has a density (d) of 0.86 to 0.95 g/cm^3;

(B) the ethylene copolymer has a MFR of 0.001 to 50 g/10 min as measured at a temperature of 190° C. and a load of 2.16 kg;

(C) the melt tension (MT) and MFR of the ethylene copolymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6; \text{ and}$$

(D) the temperature (T) at which the endothermic curve of the ethylene copolymer measured by a differential scanning calorimeter (DSC) shows the highest peak and the density (d) satisfy the relation

$$T < 400d - 250.$$

Furthermore, a first process for the preparation of an olefin polymer according to the present invention comprises polymerizing olefin in the presence of a solid catalyst formed from

(A) a compound of a transition metal in Group IVB of a periodic table, having at least two groups each having a cyclopentadienyl skeleton, said at least two groups being crosslinked through a group containing carbon and/or silicon, and

(B) an organoaluminum oxy-compound, and under the condition that the produced polymer exists in a solid state in the polymerization system, to form an olefin polymer satisfying the following conditions:

a) the olefin polymer has a MFR of 0.001 to 100 g/10 min at a temperature of 190° C. and a load of 2.16 kg; and

b) the melt tension (MT) and MFR of the olefin polymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6.$$

A first prepolymerized polyolefin-containing solid catalyst (hereinafter refer to prepolymerized solid catalyst) for olefin polymerization according to the present invention is characterized in that the solid catalyst is formed by prepolymerizing olefin in a suspension or a gas phase in the presence of a catalyst comprising

[A] a fine particle carrier,

[B] a transition metal compound (designated as a non-bridge type transition metal compound hereinafter) comprising ligands having a cyclopentadienyl skeleton, the cyclopentadienyl skeletons being not bonded mutually,

[C] a transition metal compound (designated as a bridge type metal compound) comprising at least two ligands each having a cyclopentadienyl skeleton, said at least two ligands being bonded together through an alkylene group, a substituted alkylene group, a silylene group or a substituted silylene group, and

[D] an organoaluminum oxy-compound.

A second olefin polymerization catalyst according to the present invention is characterized in that the olefin polymerization catalyst is formed from the above-described components [A], [B], [C] and [D], and [E] an organoaluminum compound.

Furthermore, a second process for the preparation of olefin polymer according to the present invention comprises polymerizing or copolymerizing olefin in the presence of the solid catalyst as described above.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows an endothermic curve obtained by measuring heat absorption of an ethylene copolymer (prepared in Example 2) of the invention using a DSC (differential scanning calorimeter).

FIG. 2 is an example of an IR spectrum of an organoaluminum oxy-compound of the invention.

FIG. 3 is an example of an IR spectrum of a known benzene-soluble organoaluminum oxy-compound.

DETAILED DESCRIPTION OF THE INVENTION

First, the ethylene copolymer according to the present invention is concretely illustrated below.

The ethylene copolymer according to the invention is a random copolymer of ethylene with an α-olefin having 3 to 20 carbon atoms. The ethylene copolymer has a density (d) of 0.86 to 0.95 g/cm^3, preferably 0.87 to 0.94 g/cm^3, more preferably 0.88 to 0.93 g/cm^3.

The density is determined by means of a density gradient tube using the strand, which has been obtained at the time of MFR measurement at 190° C. under a load of 2.16 kg, and which is heat treated by heating at 120° C. for 1 hour and slowly cooling to room temperature over a period of 1 hour.

The ethylene copolymer as described above desirably comprises constituent units (a) derived from ethylene in an amount of 55 to 99% by weight, preferably 65 to 98% by weight, more preferably 70 to 96% by weight, constituent units (b) derived from an α-olefin having 3 to 20 carbon atoms in an amount of 1 to 45% by weight, preferably 2 to 35% by weight, more preferably 4 to 30% by weight.

The composition of the copolymer is usually determined by ^{13}C-NMR spectrum analysis of a sample prepared by uniformly dissolving 200 mg of the copolymer in 1 ml of hexachlorobutadiene in a sample tube having a diameter of 10 mm under the following conditions: a measuring temperature of 120° C., a measuring frequency of 25.05 MHz, a spectrum width of 1500 Hz, a pulse repetition period of 4.2 sec and a pulse width of 6 μsec.

Examples of the α-olefin having 3 to 20 carbon atoms include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

The ethylene copolymer according to the present invention desirably has a MFR of 0.001 to 50 g/10 min, preferably 0.01 to 20 9/10 min.

The determination of the MFR is carried out in accordance with ASTM D1238-65T, under the conditions of a temperature at 190° C. and a load at 2.16 kg.

Furthermore, the melt tension (MT) and MFR of the ethylene copolymer of the invention satisfy the following relation:

$$\log MT > -0.66 \log MFR + 0.6, \text{ preferably}$$

$$\log MT > -0.66 \log MFR + 0.7, \text{ more preferably}$$

$$\log MT > -0.66 \log MFR + 0.8.$$

As described above, the ethylene copolymer of the invention is excellent in melt tension (MT), and has good moldability.

In addition, the melt tension (MT) is determined by measuring the stress of a molten copolymer while the molten copolymer is being stretched at a constant rate. That is, a produced copolymer powder or a polymer obtained by once dissolving the copolymer powder in