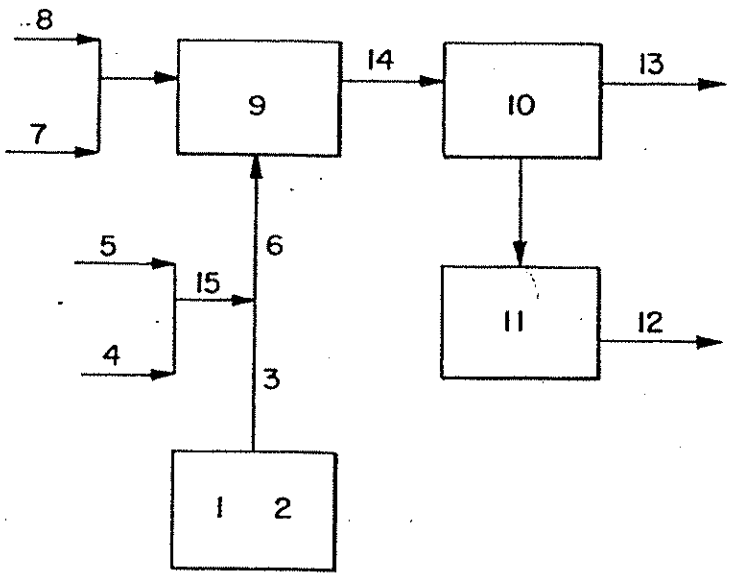
FIG. 1



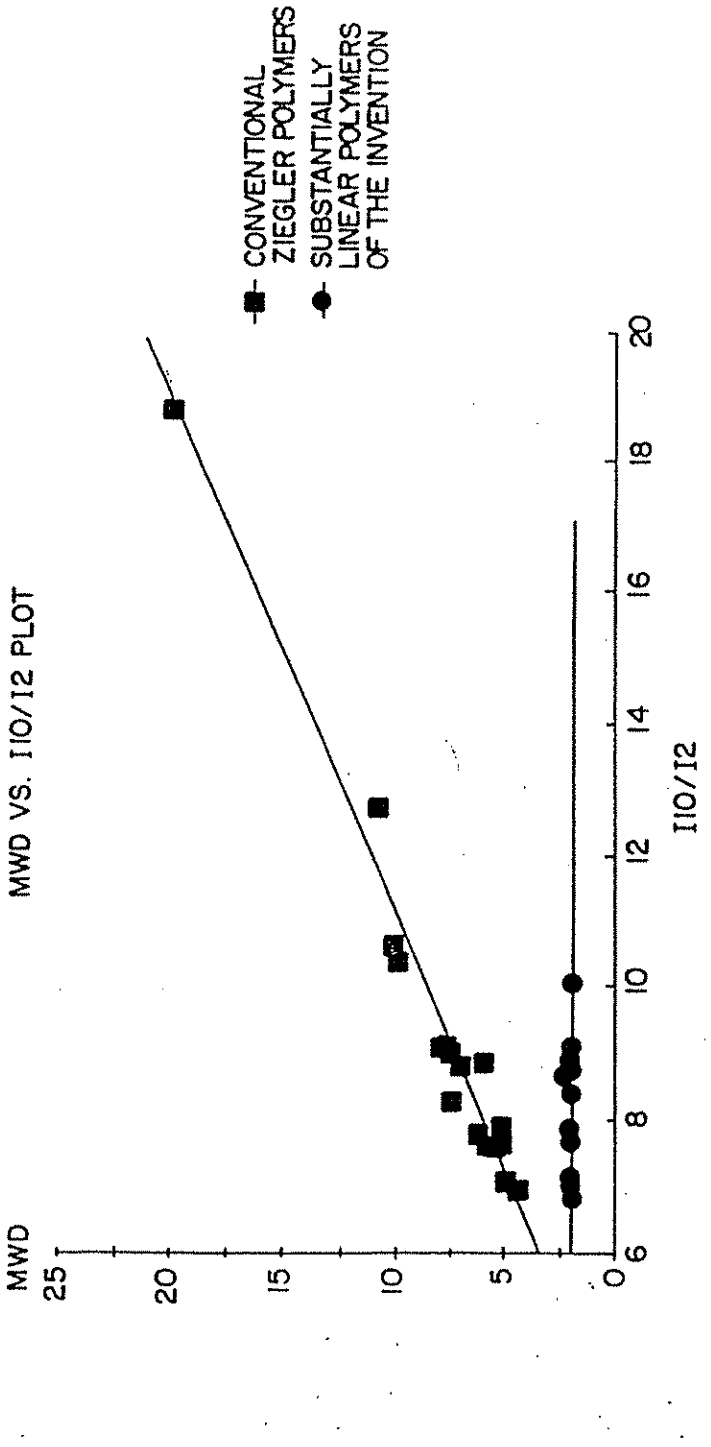

CONVENTIONAL ZIEGLER POLYMERS
SUBSTANTIALLY LINEAR POLYMERS OF THE INVENTION
MWD VS. I10/I2 PLOT
MWD
25
20
15
10
5
0
6
8
10
12
14
16
18
20
I10/I2

FIG. 2

FIG. 3

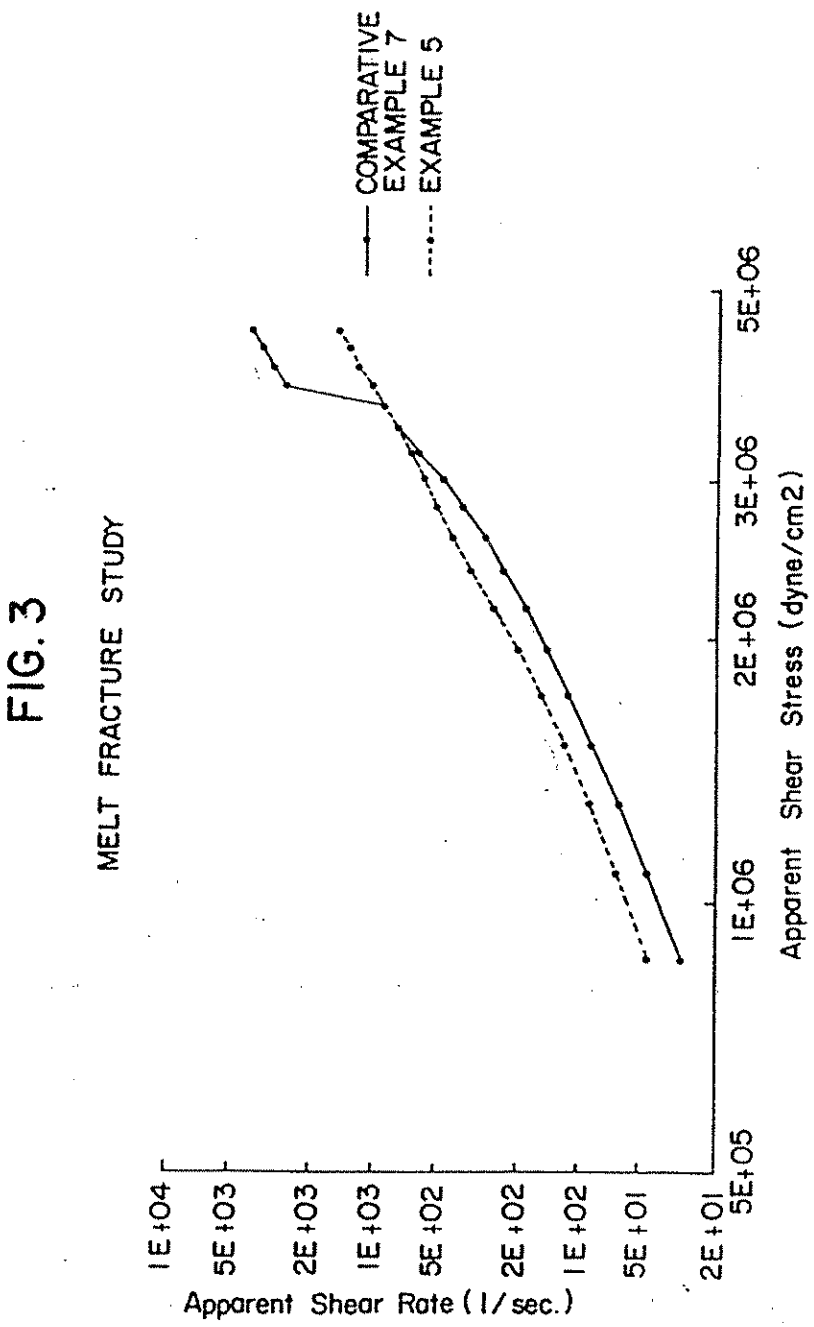
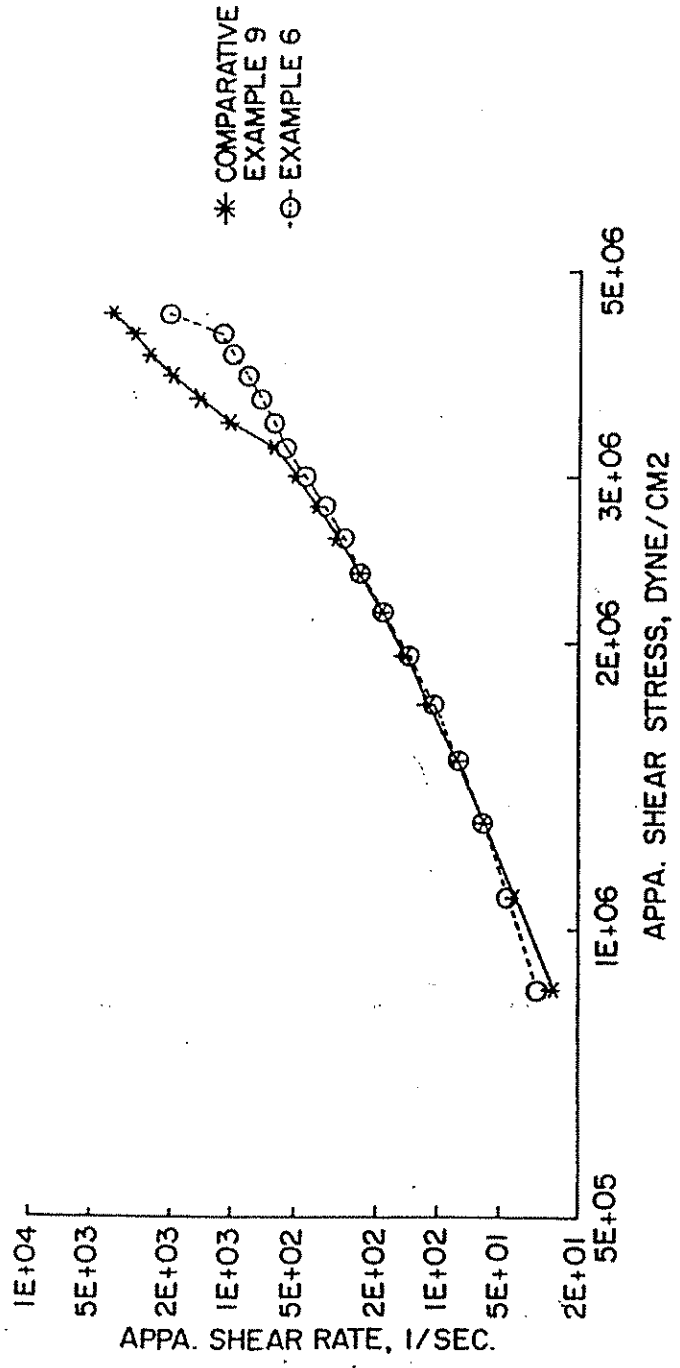

MELT FRACTURE STUDY
COMPARATIVE EXAMPLE 7
EXAMPLE 5
1E+04
5E+03
2E+03
1E+03
5E+02
2E+02
1E+02
5E+01
2E+01
Apparent Shear Rate (1/sec.)
5E+05
1E+06
2E+06
3E+06
5E+06
Apparent Shear Stress (dyne/cm2)

FIG. 4

MELT FRACTURE STUDY



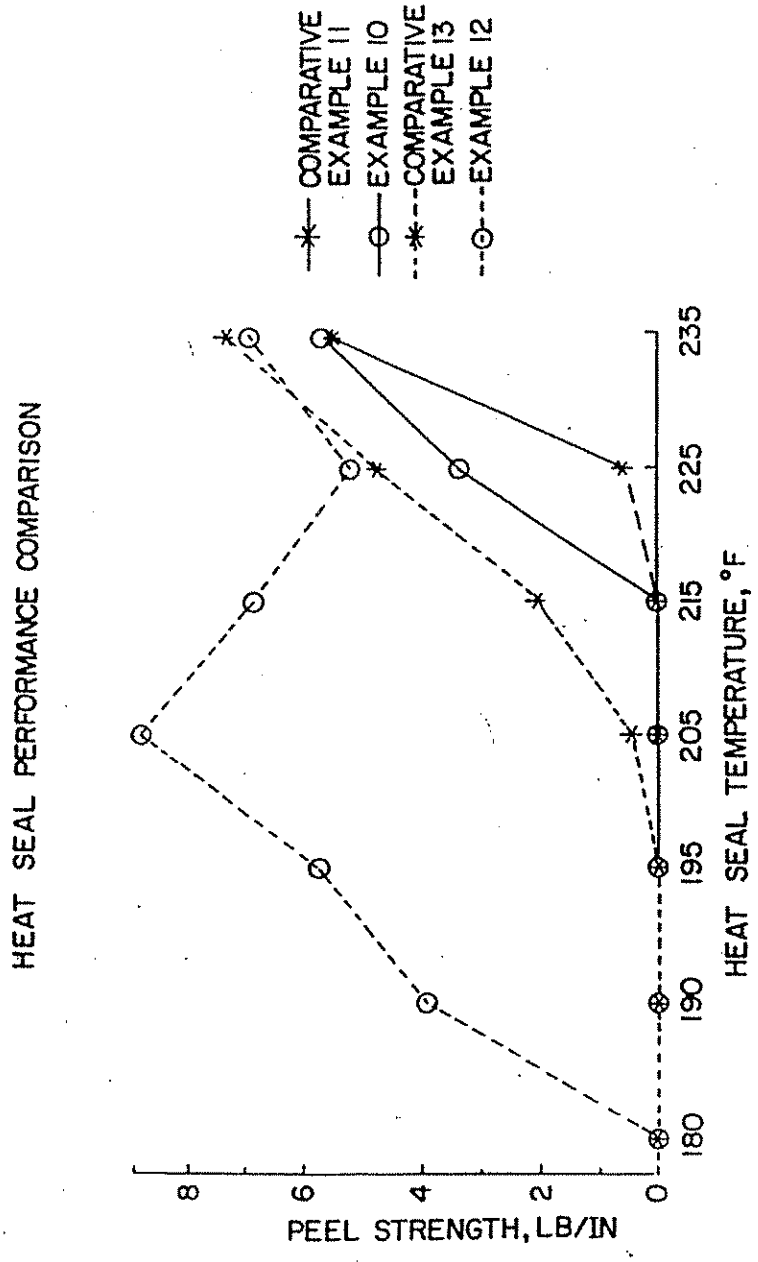


FIG. 5

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$\times 10^6$ 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$\times 10^6$ 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™ 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, ≥ 5.63,

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

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

c) a critical shear stress at onset of gross melt fracture of greater than about 4$\times 10^6$ 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 $C_{2\text{-}10}$ 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:

$$M_w = (\Sigma w_i)(M_i)$$

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™ 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;

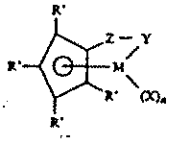
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

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

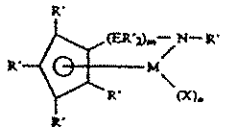
R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and

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)(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.

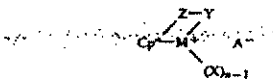
In a preferred embodiment, the metal compound is MX_{n+1}, i.e. M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. 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;

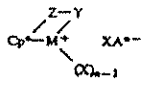
$[L-H]^+$ is a Bronsted acid;

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;

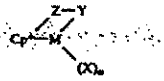
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp^* and Z together form a fused ring system;

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:



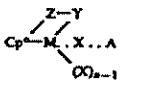
wherein:

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 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 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 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. 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 stream (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):

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

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, ≥ 5.63,

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

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

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, ≥ 5.63,

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

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

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, ≥ 5.63, and a molecular weight distribution, M_w/M_n, defined by the equation:

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

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:

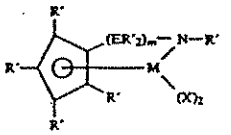
(i) a substantially linear olefin polymer, wherein the substantially linear olefin polymer is characterized as having:

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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United States Patent [19]

Chum et al.

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[45] Date of Patent: *Aug. 29, 2000

[54] FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

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Related U.S. Application Data

[63] Continuation of application No. 08/544,497, Oct. 18, 1995, Pat. No. 5,677,383, which is a continuation of application No. 08/378,998, Jan. 27, 1995, abandoned, which is a continuation of application No. 08/054,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of application No. 07/776,130, Oct. 15, 1991, Pat. No. 5,272,236, which is a continuation-in-part of application No. 07/939,281, Sep. 2, 1992, Pat. No. 5,278,272.

[51] Int. Cl.[7] C08L 23/06

[52] U.S. Cl. 525/240; 525/242; 525/320

[58] Field of Search 525/240, 242, 525/320; 526/160, 161, 352

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[57] ABSTRACT

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

16 Claims, 2 Drawing Sheets

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SPO '93, "Exact Polymers Unique Properties for Value–Added Applications" by F.J. Steininger.

FIG. 1

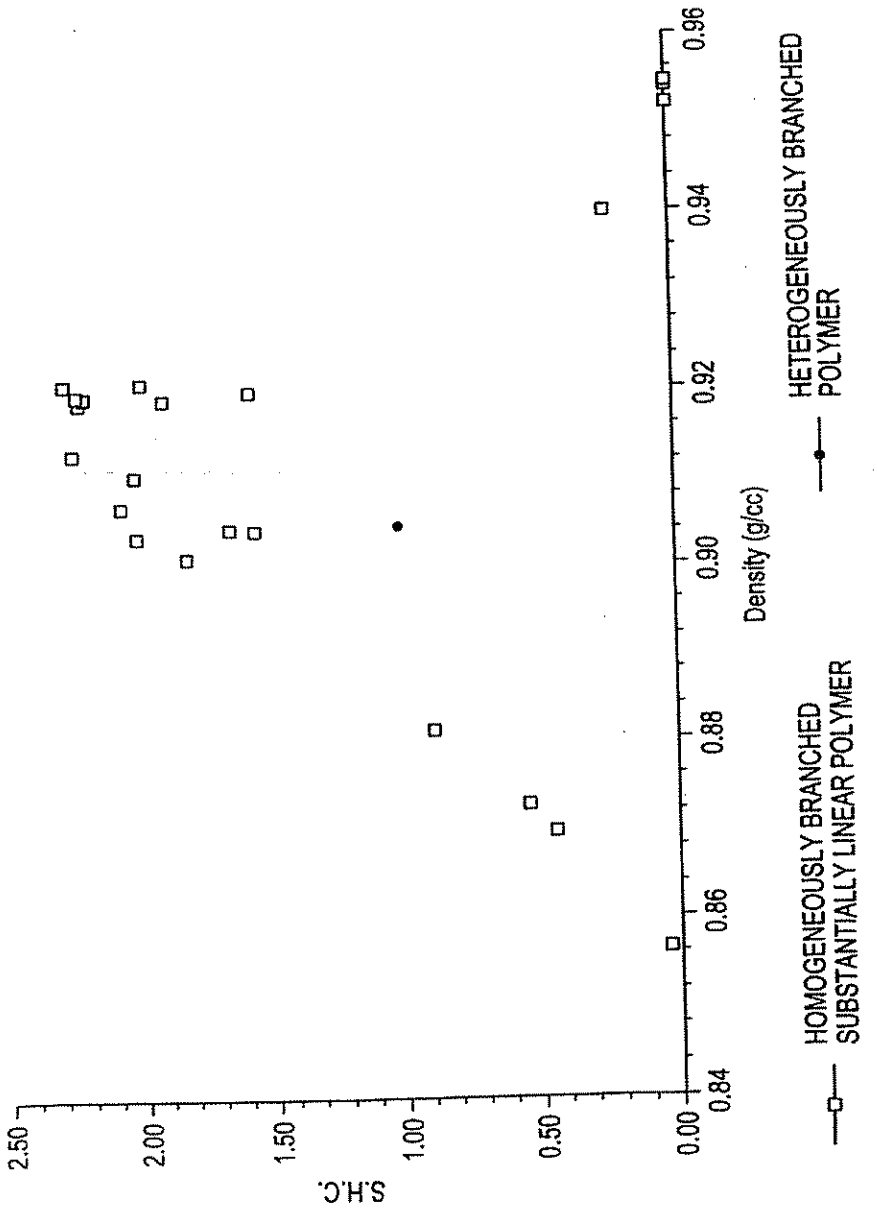
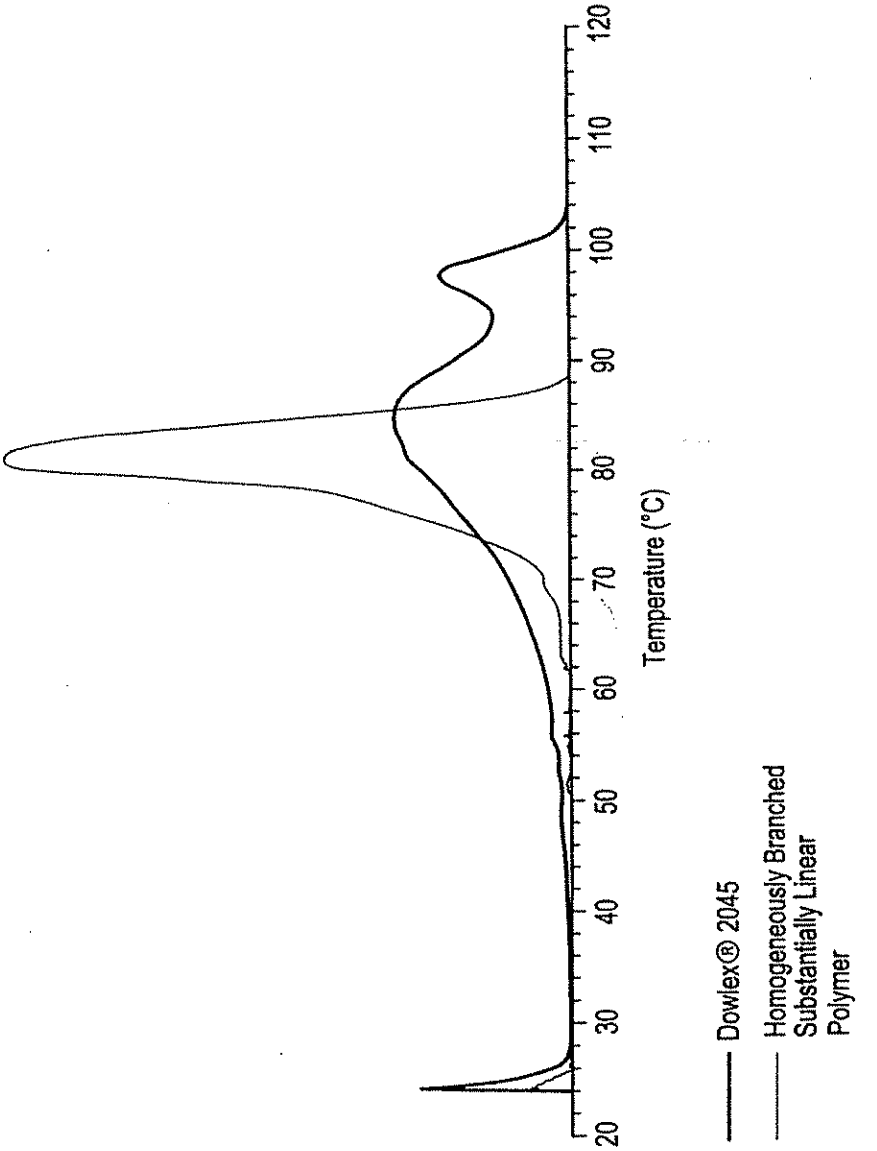

S.H.C.
2.50
2.00
1.50
1.00
0.50
0.00
0.84
0.86
0.88
0.90
0.92
0.94
0.96
Density (g/cc)
HETEROGENEOUSLY BRANCHED POLYMER
HOMOGENEOUSLY BRANCHED SUBSTANTIALLY LINEAR POLYMER

FIG. 2


20
30
40
50
60
70
80
90
100
110
120
Temperature (°C)
Dowlex® 2045
Homogeneously Branched Substantially Linear Polymer

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Rule 1.60 continuation application of application Ser. No. 08/544,497, now U.S. Pat. No. 5,677,383, filed Oct. 18, 1995 as a Rule 1.60 continuation application of abandoned application Ser. No. 08/378,998, filed Jan. 27, 1995 as a Rule 1.62 continuation application of abandoned application Ser. No. 08/054,379, filed Apr. 28, 1993 as a continuation-in-part application of application Ser. No. 07/776,130, filed Oct. 15, 1991, now U.S. Pat. No. 5,272,236 and as a continuation-in-part application of application Ser. No. 07/939,281, filed Sep. 2, 1992, now U.S. Pat. No. 5,278,272. This application is also related to application Ser. No. 08/834,050, filed Apr. 11, 1997, now issued U.S. Pat. No. 5,847,053. The disclosures of each of the above are incorporated herein, in their entireties, by reference. This application is also related to pending application Ser. No. 08/010,958, filed Jan. 29, 1993 in the names of Brian W. S. Kolthammer and Robert S. Cardwell and entitled Ethylene Interpolymerizations, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to compositions comprising specific ethylene/α-olefin polymer blends. The polymer blends preferably comprise,:

(A) at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having specific processing characteristics, blended together with

(B) a heterogeneously branched ethylene polymer.

Such compositions are particularly useful in film applications (e.g., high strength thin gauge packaging film or heat sealable packaging film).

BACKGROUND OF THE INVENTION

Thin film products fabricated from linear low density polyethylene (LLDPE) and/or high density polyethylene (HDPE) are widely used for packaging applications such as merchandise bags, grocery sacks, and industrial liners. For these applications, films with high tensile strength, as well as high impact strength, are desired because film producers can down gauge their film products and still retain packaging performance.

Previous attempts were made to optimize film tensile strength and yield strength by blending various heterogeneous polymers together on theoretical basis. While such blends exhibited a synergistic response to increase the film yield strength, the film impact strength followed the rule of mixing, often resulting in a "destructive synergism" (i.e., the film impact strength was actually lower than film made from one of the two components used to make the blend).

For example, it is known that while improved modulus linear polyethylene resin can be produced by blending high density polyethylene with a very low density polyethylene (VLDPE), the impact strength of the resin blend follows the rule of mixing.

There is a continuing need to develop polymers which can be formed into fabricated articles (e.g., film) having these combinations of properties (e.g., improved modulus, yield strength, impact strength and tear strength). The need is especially great for polymers which can be made into film which can also be down gauged without loss of strength

properties, resulting in savings for film manufacturers and consumers, as well as protecting the environment by source reduction.

Surprisingly, we have now discovered that film can have synergistically enhanced physical properties, when the film is made from a blend of at least one homogeneously branched ethylene/α-olefin interpolymer and a heterogeneously branched ethylene/α-olefin interpolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the relationship between the density and the slope of strain hardening coefficient for homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions disclosed herein, in comparison with a heterogeneously branched ethylene/α-olefin copolymer.

FIG. 2 shows the short chain branching distribution (as measured by analytical temperature rising elution fractionation (ATREF)) for a homogeneously branched substantially linear ethylene/1-octene copolymer used in the invention, in comparison with Dowlex™ 2045 (a heterogeneously branched ethylene/1-octene copolymer made by The Dow Chemical Company).

SUMMARY OF THE INVENTION

Formulated ethylene/α-olefin compositions have now been discovered to have improved physical and mechanical strength and are useful in making fabricated articles. Films made from these novel compositions exhibit surprisingly good impact and tensile properties, and an especially good combination of modulus, yield, ultimate tensile, and toughness (e.g., Dart impact).

The compositions comprise (A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

In another aspect, the compositions comprise from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of:

(A) at least one homogeneously branched linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

Preferably, both the homogeneously branched substantially linear ethylene/α-olefin interpolymer and the homogeneously branched linear ethylene/α-olefin interpolymer each have a slope of strain hardening coefficient greater than or equal to about 1.3.

DETAILED DESCRIPTION OF THE INVENTION

The homogeneously branched ethylene/α-olefin interpolymer is preferably a homogeneously branched substantially linear ethylene/α-olefin interpolymer as described in pending U.S. Ser. No. 07/776,130. The homogeneously branched ethylene/α-olefin interpolymer can also be a linear ethylene/α-olefin interpolymer as described in U.S. Pat. No. 3,645,992 (Elston), the disclosure of which is incorporated herein by reference.

The substantially linear ethylene/α-olefin interpolymers are not "linear" polymers in the traditional sense of the term, as used to describe linear low density polyethylene (e.g., Ziegler polymerized linear low density polyethylene (LLDPE)), nor are they highly branched polymers, as used to describe low density polyethylene (LDPE).

The substantially linear ethylene/α-olefin interpolymers of the present invention are herein defined as in copending application U.S. Ser. No. 07/776,130 and in copending application entitled "Elastic Substantially Linear Olefin Polymers" filed Sep. 2, 1992 in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens.

The homogeneously branched ethylene/α-olefin interpolymers useful for forming the compositions described herein are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The homogeneity of the interpolymers is typically described by the SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) and 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), in U.S. Pat. No. 4,798,081 (Hazlitt et al.), or in U.S. Pat. No. 5,089,321 (Chum et al.) the disclosures of all of which are incorporated herein by reference. The SCBDI or CDBI for the linear and for the substantially linear olefin polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent. The homogeneous ethylene/α-olefin polymers used in this invention essentially lack a measurable "high density" fraction as measured by the TREF technique (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls/1000 carbons). The homogeneously branched ethylene/α-olefin polymers also do not contain any highly short chain branched fraction (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching equal to or more than about 30 methyls/1000 carbons).

The substantially linear ethylene/α-olefin interpolymers for use in the present invention typically are interpolymers of ethylene with at least one C_3–C_{20} α-olefin and/or C_4–C_{18} diolefins. Copolymers of ethylene and 1-octene are especially preferred. The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like. That is, at least one other comonomer is polymerized with ethylene to make the interpolymer. Ethylene copolymerized with two or more comonomers can also be used to make the homogeneously branched substantially linear interpolymers useful in this invention. Preferred comonomers include the C_3–C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

The term "linear ethylene/α-olefin interpolymer" means that the interpolymer does not have long chain branching. That is, the linear ethylene/α-olefin interpolymer has an absence of long chain branching, as for example the linear low density polyethylene polymers or linear high density polyethylene polymers made using uniform (i.e., homogeneous) branching distribution polymerization processes (e.g., as described in U.S. Pat. No. 3,645,992 (Elston)) and are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The term "linear ethylene/α-olefin interpolymer" does not refer to high pressure branched (free-radical polymerized) polyethylene which , is known to those skilled in the art to have numerous long chain branches. The branching distribution of the homogeneously branched linear ethylene/α-olefin interpolymers is the same or substantially the same as that described for the homogeneously branched substantially linear ethylene/α-olefin interpolymers, with the exception that the linear ethylene/α-olefin interpolymers do not have any long chain branching. The homogeneously branched linear ethylene/α-olefin interpolymers comprise ethylene with at least one C_3–C_{20} α-olefin and/or C_4–C_{18} diolefin. Copolymers of ethylene and 1-octene are especially preferred. Preferred comonomers include the C_3–C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

Both the homogeneously branched substantially linear and linear ethylene/α-olefin interpolymers have a single melting point, as opposed to traditional heterogeneously branched Ziegler polymerized ethylene/α-olefin copolymers having two or more melting points, as determined using differential scanning calorimetry (DSC).

The density of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally from about 0.89 g/cm^3 to about 0.935 g/cm^3, preferably from about 0.905 g/cm^3 to about 0.925 g/cm^3, and especially from about 0.905 g/cm^3 to less than about 0.92 g/cm^3.

The amount of the homogeneously branched linear or substantially linear ethylene/α-olefin polymer incorporated into the composition varies depending upon the heterogeneously branched ethylene polymer to which it is combined. However, about 50 percent (by weight of the total composition) of the homogeneous linear or substantially linear ethylene/α-olefin polymer is especially preferred in the novel compositions disclosed herein.

The molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers for use in the present invention is conveniently indicated using a melt index measurement according to ASTM

D-1238, Condition 190° C./2.16 kg (formerly 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 lower melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers useful herein is generally about 0.001 grams/10 minutes (g/10 min). The upper melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is about 10 g/10 min, preferably less than about 1 g/10 min, and especially less than about 0.5 g/10 min.

Another measurement useful in characterizing the molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190° C./10 kg (formerly known as "Condition (N)" and also known as I_{10}). The ratio of the I_{10} and I_2 melt index terms is the melt flow ratio and is designated as I_{10}/I_2. Generally, the I_{10}/I_2 ratio for the homogeneously branched linear ethylene/α-olefin interpolymers is about 5.6. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, i.e., the higher the I_{10}/I_2 ratio, the more long chain branching in the interpolymer. Generally, the I_{10}/I_2 ratio of the homogeneously branched substantially linear ethylene/α-olefin interpolymers is at least about 6, preferably at least about 7, especially at least about 8 or above. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers, the higher the I_{10}/I_2 ratio, the better the processability.

Other additives such as antioxidants (e.g., hindered phenolics (e.g., Irganox® 1010 made by Ciba Geigy Corp.), phosphites (e.g., Irgafos® 168 also made by Ciba Geigy Corp.)), cling additives (e.g., PIB), antiblock additives, pigments, fillers, and the like can also be included in the formulations, to the extent that they do not interfere with the enhanced formulation properties discovered by Applicants.

MOLECULAR WEIGHT DISTRIBUTION DETERMINATION

The molecular weight distribution of the linear or substantially linear olefin interpolymer product samples is analyzed by gel permeation chromatography (GPC) on a Waters 150C 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 milliliter/minute and the injection size is 200 microliters. A differential refractometer is being used as the detector.

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 ith fraction eluting from the GPC column.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin polymers, the molecular weight distribution (M_w/M_n) is preferably from about 1.8 to about 2.8, more preferably from about 1.89 to about 2.2 and especially about 2.

DETERMINATION OF CRITICAL SHEAR STRESS AND CRITICAL SHEAR RATE

Gas extrusion rheometry (GER) 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." 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 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. Preferably, the critical shear stress at the OGMF and the critical shear stress at the OSMF for the substantially linear ethylene polymers [described] used herein is greater than about 4×10^6 dyne/cm^2 and greater than about 2.8×10^6 dyne/ cm^2, respectively.

DETERMINATION OF THE SLOPE OF STRAIN HARDENING COEFFICIENT

The slope of strain hardening is measured by compression molding a plaque from the polymer to be tested. Typically, the plaque is molded at about 177° C. for 4 minutes under almost no pressure and then pressed for 3 minutes under a pressure of about 200 psi. The plaque is then allowed to cool at about 8° C./minute while still under 200 psi pressure. The molded plaque has a thickness of about 0.005 inches. The plaque is then cut into a dogbone shaped test piece using a steel rule die. The test piece is 0.315 inches wide and 1.063 inches long. The start of the curved portion of the dogbone shape begins at 0.315 inches from each end of the sample and gently curves (i.e., tapers) to a width of 0.09 inches. The curve ends at a point 0.118 inches from the start of the curve

such that the interior portion of the dogbone test piece has a width of 0.09 inches and a length of 0.197 inches.

The tensile properties of the test sample is tested on an Instron Tensile Tester at a crosshead speed of 1 inch/minute. The slope of strain hardening is calculated from the resulting tensile curve by drawing a line parallel to the strain hardening region of the resulting stress/strain curve. The strain hardening region occurs after the sample has pulled its initial load ((i.e., stress) usually with little or no elongation during the initial load) and after the sample has gone through a slight drawing stage (usually with little or no increase in load, but with increasing elongation (i.e., strain)). In the strain hardening region, the load and the elongation of the sample both continue to increase. The load increases in the strain hardening region at a much lower rate than during the initial load region and the elongation also increase, again at a rate lower than that experienced in the drawing region. FIG. 1 shows the various stages of the stress/strain curve used to calculate the slope of strain hardening. The slope of the parallel line in the strain hardening region is then determined.

The slope of strain hardening coefficient (SHC) is calculated according to the following equation:

$$SHC=(\text{slope of strain hardening})*(I_2)^{0.25}$$

where I_2=melt index in grams/10 minutes.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin interpolymers used in the invention, the SHC is greater than about 1.3, preferably greater than about 1.5.

Surprisingly, the slope of strain hardening coefficient reaches a maximum for the linear or the substantially linear ethylene/α-olefin polymers at a density from about 0.89 g/cm^3 to about 0.935 g/cm^3. Heterogeneous ethylene/α-olefin polymers, in contrast, do not behave in the same manner. FIG. 1 graphically depicts the relationship between the density of the homogeneously branched substantially linear ethylene polymers and ethylene/α-olefin polymers as a function of their slope of strain hardening coefficient, and includes a heterogeneously branched ethylene/1-octene copolymer (polymer W** in Table 1) for comparison purposes. Table 1 displays the data of FIG. 1 in tabular form:

TABLE 1

Polymer	Melt Index (I_2) (g/10 min)	Density (g/cm^3)	I_{10}/I_2	SHC*
A	1	0.8564	7.36	0.004
B	1.03	0.8698	7.46	0.45
C	0.57	0.873	7.22	0.54
D	1.01	0.8817	7.36	0.89
E	1.06	0.9018	7.61	1.84
F	2.01	0.9041	8.07	2.03
G	0.77	0.9047	9.01	1.57
H	9.82	0.9048	7.05	1.67
I	4.78	0.9077	7.16	2.08
J	3.13	0.9113	7.67	2.04
K	2.86	0.9139	7.87	2.27
L	1.08	0.9197	8.07	2.24
M	0.96	0.9198	9.61	1.93
N	0.99	0.9203	9.09	2.25
O	1.11	0.9204	10.15	1.59
P	1.06	0.9205	9.08	2.25
Q	1.12	0.9216	8.94	2.3
R	30.74	0.9217	6.27	2
S	31.58	0.94	6.02	0.24
T	0.97	0.9512	12.11	0
U	0.97	0.9533	10.5	0
V	0.92	0.954	7.39	0
W**	0.8	0.905	8.7	1.02

*SHC = Slope of Strain Hardening Coefficient
**A comparative heterogeneously branched ethylene/1-octene copolymer

THE HETEROGENEOUSLY BRANCHED ETHYLENE POLYMER

The ethylene polymer to be combined with the homogeneous ethylene/α-olefin interpolymer is a heterogeneously branched (e.g., Ziegler polymerized) interpolymer of ethylene with at least one C_3–C_{20} α-olefin (e.g., linear low density polyethylene (LLDPE)).

Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution. For example, heterogeneously branched LLDPE polymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene). The amount of each of these fractions varies depending upon the whole polymer properties desired. For example, linear homopolymer polyethylene has neither branched nor highly branched fractions, but is linear. A very low density heterogeneous polyethylene having a density from about 0.9 g/cm^3 to about 0.915 g/cm^3 (such as Attane® copolymers, sold by The Dow Chemical Company and Flexomer® sold by Union Carbide Corporation) has a higher percentage of the highly short chain branched fraction, thus lowering the density of the whole polymer.

Heterogeneously branched LLDPE (such as Dowlex® sold by The Dow Chemical Company) has a lower amount of the highly branched fraction, but has a greater amount of the medium branched fraction. FIG. 2 graphically depicts the relative amounts of these various fractions (as measured using temperature rising elution fractionation) for Dowlex® 2045 (a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.93 and a molecular weight distribution (M_w/M_n) of about 3.34), as compared with a homogeneously branched substantially linear ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10.5 and a molecular weight distribution (M_w/M_n) of about 2.18. Note that the homogeneously branched polymer has a single relatively narrow peak at an elution temperature of about 85° C., while the Dowlex® 2045 polymer has a broad branching distribution, as represented by the breadth of elution temperatures over which the polymer fractions elute. Dowlex® 2045 also has a distinct peak at an elution temperature of about 98° C., indicating the "linear" fraction of the whole polymer. Increasing the fraction of the polymer which has the beneficial properties, without concomitantly increasing other fractions has not been demonstrated here-to-fore.

Preferably, however, the heterogeneously branched ethylene polymer is a heterogeneously branched Ziegler polymerized ethylene/α-olefin interpolymer having no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≅1.3.

More preferably, the heterogeneously branched ethylene polymer is a copolymer of ethylene with a C_3–C_{20} α-olefin, wherein the copolymer has:

(i) a density from about 0.93 g/cm^3 to about 0.965 g/cm^3,

(ii) a melt index (I_2) from about 0.1 g/10 min to about 500 g/10 min, and

(iii) no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1.3.

The heterogeneously branched ethylene/α-olefin interpolymers and/or copolymers also have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC).

THE FORMULATED COMPOSITIONS

The compositions disclosed herein can be formed by any convenient method, including dry blending the individual components and subsequently melt mixing or by pre-melt mixing in a separate extruder (e.g., a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a twin screw extruder).

Another technique for making the compositions in-situ is disclosed in pending U.S. Ser. No. 08/010,958, entitled Ethylene Interpolymerizations, which was filed Jan. 29, 1993 in the names of Brian W. S. Kolthammer and Robert S. Cardwell, the disclosure of which is incorporated herein in its entirety by reference. U.S. Ser. No. 08/010,958 describes, inter alia, interpolymerizations of ethylene and C_3–C_{20} alpha-olefins using a homogeneous catalyst in at least one reactor and a heterogeneous catalyst in at least one other reactor. The reactors can be operated sequentially or in parallel.

The compositions can also be made by fractionating a heterogeneous ethylene/α-olefin polymer into specific polymer fractions with each fraction having a narrow composition (i.e., branching) distribution, selecting the fraction having the specified properties (e.g., SHC≧1.3), and blending the selected fraction in the appropriate amounts with another ethylene polymer. This method is obviously not as economical as the in-situ interpolymerizations of U.S. Ser. No. 08/010,958, but can be used to obtain the compositions of the invention.

FABRICATED ARTICLES MADE FROM THE NOVEL COMPOSITIONS

Many useful fabricated articles benefit from the novel compositions disclosed herein. For example, molding operations can be used to form useful fabricated articles or parts from the compositions disclosed herein, including various injection molding processes (e.g., that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 264–268, "Introduction to Injection Molding" by H. Randall Parker and on pp. 270–271, "Injection Molding Thermoplastics" by Michael W. Green, the disclosures of which are incorporated herein by reference) and blow molding processes (e.g., that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 217–218, "Extrusion-Blow Molding" by Christopher Irwin, the disclosure of which is incorporated herein by reference), profile extrusion, calandering, pultrusion (e.g., pipes) and the like. Rotomolded articles can also benefit from the novel compositions described herein. Rotomolding techniques are well known to those skilled in the art and include, for example, those described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 296–301, "Rotational Molding" by R. L. Fair, the disclosure of which is incorporated herein by reference).

Fibers (e.g., staple fibers, melt blown fibers or spunbonded fibers (using, e.g., systems as disclosed in U.S. Pat. Nos. 4,340,563, 4,663,220, 4,668,566, or 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)) can also be made from the novel compositions disclosed herein.

Film and film structures particularly benefit from the novel compositions described herein and can be made using conventional hot blown film fabrication techniques or other biaxial orientation processes such as tenter frames or double bubble processes. Conventional hot blown film processes are described, for example, in *The Encyclopedia of Chemical Technology*, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416–417 and Vol. 18, pp. 191–192, the disclosures of which are incorporated herein by reference. Biaxial orientation film manufacturing process such as described in a "double bubble" process as in U.S. Pat. No. 3,456,044 (Pahlke), and the processes described in U.S. Pat. No. 4,352,849 (Mueller), U.S. Pat. No. 4,597,920 (Golike), U.S. Pat. No. 4,820,557 (Warren), U.S. Pat. No. 4,837,084 (Warren), U.S. Pat. No. 4,865,902 (Golike et al.), U.S. Pat. No. 4,927,708 (Herran et al.), U.S. Pat. No. 4,952,451 (Mueller), U.S. Pat. No. 4,963,419 (Lustig et al.), and U.S. Pat. No. 5,059,481 (Lustig et al.), the disclosures of each of which are incorporated herein by reference, can also be used to make film structures from the novel compositions described herein. The film structures can also be made as described in a tenter-frame technique, such as that used for oriented polypropylene.

Other multi-layer film manufacturing techniques for food packaging applications are described in *Packaging Foods With Plastics*, by Wilmer A. Jenkins and James P. Harrington (1991), pp. 19–27, and in "Coextrusion Basics" by Thomas I. Butler, *Film Extrusion Manual: Process, Materials, Properties* pp. 31–80 (published by TAPPI Press (1992)) the disclosures of which are incorporated herein by reference.

The films may be monolayer or multilayer films. The film made from the novel compositions can also be coextruded with the other layer(s) or the film can be laminated onto another layer(s) in a secondary operation, such as that described in *Packaging Foods With Plastics*, by Wilmer A. Jenkins and James P. Harrington (1991) or that described in "Coextrusion For Barrier Packaging" by W. J. Schrenk and C. R. Finch, *Society of Plastics Engineers RETEC Proceedings*, June 15–17 (1981), pp. 211–229, the disclosure of which is incorporated herein by reference. If a monolayer film is produced via tubular film (i.e., blown film techniques) or flat die (i.e., cast film) as described by K. R. Osborn and W. A. Jenkins in "Plastic Films, Technology and Packaging Applications" (Technomic Publishing Co., Inc (1992)), the disclosure of which is incorporated herein by reference, then the film must go through an additional post-extrusion step of adhesive or extrusion lamination to other packaging material layers to form a multilayer structure. If the film is a coextrusion of two or more layers (also described by Osborn and Jenkins), the film may still be laminated to additional layers of packaging materials, depending on the other physical requirements of the final film. "Laminations Vs. Coextrusion" by D. Dumbleton (Converting Magazine (September 1992), the disclosure of which is incorporated herein by reference, also discusses lamination versus coextrusion. Monolayer and coextruded

films can also go through other post extrusion techniques, such as a biaxial orientation process.

Extrusion coating is yet another technique for producing multilayer film structures using the novel compositions described herein. The novel compositions comprise at least one layer of the film structure. Similar to cast film, extrusion coating is a flat die technique. A sealant can be extrusion coated onto a substrate either in the form of a monolayer or a coextruded extrudate.

Generally for a multilayer film structure, the novel compositions described herein comprise at least one layer of the total multilayer film structure. Other layers of the multilayer structure include but are not limited to barrier layers, and/or tie layers, and/or structural layers. Various materials can be used for these layers, with some of them being used as more than one layer in the same film structure. Some of these materials include: foil, nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic add (EMAA) copolymers, LLDPE, HDPE, LDPE, nylon, graft adhesive polymers (e.g., maleic anhydride grafted polyethylene), and paper. Generally, the multilayer film structures comprise from 2 to about 7 layers.

EXAMPLE 1

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.91 g/cm^3, I_{10}/I_2 of about 10, M_w/M_n of about 2, and SHC of about 1.81 is dry blended and then melt blended with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC≧1.3. The dry blend is tumble blended in a 50 gallon drum for about 1 hour.

The melt blend is produced in a ZSK 30 twin screw extruder (30 mm screw diameter) and is then fabricated into film. The final blended composition has a density of about 0.919 g/cm^3.

The blended composition is then fabricated into blown film having a thickness of about 1 mil on an Egan Blown Film Line having a 2 inch diameter screw, a 3 inch die and at a 2.5 inch blow up ratio (BUR), as described in Table 2. For all film samples in Examples 1, 2,4, and 6 and for comparative examples 3, 5, and 7, the targeted gauge is about 1 mil, using a blow-up ratio (BUR) of 2.5:1, a LLDPE screw design is used, a die gap of 70 mils is used, and a lay flat of about 11.875 inches is used.

Film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples. Dart impact (type A) of the films is measured in accordance with ASTM D-1709-85; tensile strength, yield, toughness, and 2% secant modulus of the films is measured in accordance with ASTM D-882; Elmendorf tear (type B) is measured in accordance with ASTM D-1922; PPT tear is measured in accordance with ASTM D-2582; Block is measured in accordance with ASTM D-3354.

Puncture is measured by using an Instron tensiometer Tensile Tester with an integrator, a specimen holder that holds the film sample taut across a circular opening, and a rod-like puncturing device with a rounded tip (ball) which is attached to the cross-head of the Instron and impinges perpendicularly onto the film sample. The Instron is set to obtain a crosshead speed of 10 inches/minute and a chart speed (if used) of 10 inches/minute. Load range of 50% of the load cell capacity (100 lb. load for these tests) should be used. The puncturing device is installed to the Instron such that the damping unit is attached to the lower mount and the ball is attached to the upper mount on the crosshead. Six film specimens are used (each 6 inches square). The specimen is damped in the film holder and the film holder is secured to the mounting bracket. The crosshead travel is set and continues until the specimen breaks. Puncture resistance is defined as the energy to puncture divided by the volume of the film under test. Puncture resistance (PR) is calculated as follows:

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

where

PR=puncture resistance (ft-lbs/in^3)

E=energy (inch-lbs)=area under the load displacement curve

12=inches/foot

T=film thickness (inches), and

A=area of the film sample in the damp=12.56 in^2.

EXAMPLE 2

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 0.5 g/10 min, density of about 0.915 g/cm^3, I_{10}/I_2 of about 11, M_w/M_n of about 2.4, and SHC of about 2.265 is dry blended and then melt blended (as described in Example 1) with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC≧1.3. The final blended composition has a density of about 0.92 g/cm^3.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

COMPARATIVE EXAMPLE 3

A heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.92 g/cm^3, I_{10}/I_2 of about 7.93, and M_w/M_n of about 3.34 is made into film as described in Example 1. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 36 percent (by weight of the heterogeneous copolymer) having a SHC≧1.3. The entire heterogeneous ethylene/1-octene copolymer has a SHC of about 1.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

EXAMPLE 4

Example 4 is an in-situ blend made according to U.S. Ser. No. 08/010,958, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene copolymer having a melt index (I_2) of about 0.5 g/10 min., and a density of about 0.9054 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8.27 and a molecular weight distribution (M_w/M_n) of about 1.979 and comprises about

50% (by weight of the total composition). A heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 1.5 g/10 min., and a density of about 0.944 g/cm^3 and comprises the remaining 50% (by weight of the total composition). The total composition has a melt index (I_2) of about 1 g/10 min., a density of about 0.9248 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.22 and a molecular weight distribution (M_w/M_n) of about 2.641. This composition is made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 5

Comparative Example 5 is an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375, filed Oct. 7, 1991, the disclosure of which is incorporated herein by reference. About 15% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.56 g/10 min., a density of about 0.9256 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 9.5 and a molecular weight distribution (M_w/M_n) of about 4.35. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

EXAMPLE 6

Example 6 is an in-situ blend made according to U.S. Ser. No. 08/010,958, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene-copolymer having a fractional melt index (I_2), a density of about 0.906 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8–10 and a molecular weight distribution (M_w/M_n) of about 2.2 and comprises about 43% (by weight of the total composition). A second heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 0.85 g/10 minutes, a density of about 0.938 g/cm^3 and comprises the remaining 57% (by weight of the total composition). The total composition has a melt index (I_2) of about 0.53 g/10 minutes, a density of about 0.9246 g/cm^3 a melt flow ratio (I_{10}/I_2) of about 7.83, and a molecular weight distribution (M_w/M_n) of about 2.8. This composition is made into blown film as described in Table 2 and the film properties are reported in Table 3.

COMPARATIVE EXAMPLE 7

Comparative Example 7 is an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375, filed Oct. 7, 1991, the disclosure of which is incorporated herein by reference. About 25% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.49 g/10 min., a density of about 0.9244 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10 and a molecular weight distribution (M_w/M_n) of about 4.78. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 8

Comparative example 8 is a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 minutes, a density of about 0.9249 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8 and a molecular weight distribution (M_w/M_n) of about 3.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and comparative examples.

TABLE 2

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Zone 1A (° F.)	300	300	300	300	300	300	300	300
Zone 1B (° F.)	450	451	475	474	475	475	475	474
Zone 1C (° F.)	450	450	475	475	475	475	475	475
Zone 2A (° F.)	450	450	475	474	475	475	475	475
Zone 2B (° F.)	450	450	455	475	475	475	475	475
Zone 2C (° F.)	450	450	475	475	475	475	475	475
Zone 3 (° F.)	451	452	474	477	477	476	476	474
Zone 4 (° F.)	450	450	473	475	475	475	475	475
Zone 5 (° F.)	450	450	475	475	475	475	475	475
Melt temp. (° F.)	475	477	515	501	502	499	499	497
Blower Air temp. (° F.)	47.3	45.7	57	44.4	86.5	47.6	NA	47.3
Chill Water temp. (° F.)	39	37.6	51.1	38.3	86.8	40	38.7	40.5
Extruder Die press. (psi)	2843	3427	1321	1874	1763	2883	2525	1952
Nozzle press. (in.)	3.2	4.5	4.38	4.4	4.9	4.6	4.6	4.3
Amps	27.3	33.1	37.7	39.9	40.2	50.1	42.6	38.6
Extruder speed (rpm)	27.6	28.8	21.5	23.1	21.1	21.5	22.1	21.7
Nip Roll speed (rpm)	33.1	36.9	39	39.8	36.2	37	36	37.8
Output (lbs/hr)	31	NR*	38.3	39	NR*	36	36	36
Frost line height (in.)	12.5	9	15	12	12	10.5	11	10.5

*NR = Not recorded

TABLE 3

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Yield (MD*) (psi)	1605	1595	1645	2040	2243	1973	1810	1782
Tensile (MD*) (psi)	8522	9525	7444	7794	7931	9325	8455	4928
Toughness (MD*) (ft-lbs/in^3)	1689	1773	1439	1671	1519	NR	NR	NR
Yield (CD**) (psi)	1530	1489	1706	2267	2407	1997	1809	1832
Tensile (CD**) (psi)	6252	7603	5807	7079	7458	7153	6326	4598
Toughness (CD**) (ft-lbs/in^3)	1282	1599	1358	1656	1495	NR	NR	NR
Elmendorf B(MD*) (grams)	288	216	334	317	194	320	398	297
Elmendorf B (CD**) (grams)	621	566	413	630	664	640	621	527
PPT Tear (MD*) (lbs.)	6.79	6.18	5.99	6.2	6.5	6.2	6.2	5.3
PPT Tear (CD**) (lbs.)	7.44	7.42	6.46	6.8	8.1	7.0	7.5	6.1
Dart Impact A (grams)	708	610	354	410	186	412	186	164
Puncture (ft-lbs/in^3)	316	349	251	231	256	250	227	237
Film Block g.	75	33	87	32	17	11.8	17	22
Film Gradient Density (g/cm^3)	0.9145	0.9153	0.9155	0.9205	0.9218	0.9198	0.9201	0.9207
Film Gauge (low) (mils)	0.9	0.9	0.9	0.85	0.8	0.98	0.95	1.05
Film Gauge (high) (mils)	1.2	1.05	1.1	0.95	1	1.08	1.05	1.15

*MD = Machine direction
**CD = Cross direction
NR = Not Recorded

In general, films made from the novel formulated ethylene/α-olefin compositions exhibit good impact and tensile properties, and an especially good combination of tensile, yield and toughness (e.g., toughness and dart impact). Further, films from the example resins exhibited significant improvements over films made from the comparative resins in a number of key properties.

For example, comparing examples 1 and 2 with comparative example 3, the data show films produced from the melt blends (examples 1 and 2) exhibited significantly higher values for the following film properties: dart impact, MD tensile, CD tensile, MD toughness, CD toughness MD ppt tear, CD ppt tear, CD Elmendorf tear B, puncture and significantly lower block.

Comparing example 4 to comparative example 5, the data show films produced from the in-situ blend (made according to U.S. Ser. No. 08/010.958) exhibited significantly higher values for the following film properties: dart impact, MD toughness and CD toughness.

Comparing example 6 to comparative examples 7 (an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375) and 8 (an heterogeneously branched ethylene/1-octene copolymer), the data show films produced from the in-situ blend (made according to U.S. Ser. No. 08/010,958) exhibited significantly higher values for the following film properties: dart impact, md yield, cd yield, md tensile, cd tensile, cd Elmendorf tear b and puncture and significantly lower block.

We claim:

1. An ethylene polymer composition comprising

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one ethylene interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.935 g/cm^3,

(ii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iii) a slope of strain hardening coefficient greater than or equal to 1.3, and

(iv) a Composition Distribution Branch Index (CDBI) greater than 50 percent; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one ethylene polymer characterized as having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and comprising a linear polymer fraction, as determined using a temperature rising elution fractionation (TREF) technique.

2. The composition of claim 1 wherein the ethylene interpolymer (A) has a slope of strain hardening coefficient greater than or equal to 1.5.

3. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography.

4. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

5. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a single melting point, as determined using differential scanning calorimetry.

6. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

7. The composition of claim 1 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and a single melting point as determined using differential scanning calorimetry.

8. The composition of claim 1 or claim 3 wherein the ethylene interpolymer (A) is further characterized as having a no high density polymer fraction, as determined using a temperature rising elution fractionation technique, and a single melting point, as determined using differential scanning calorimetry.

9. A film made from an ethylene polymer composition, wherein the composition comprises

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one ethylene interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.935 g/cm^3,

(ii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iii) a slope of strain hardening coefficient greater than or equal to 1.3, and

(iv) a Composition Distribution Branch Index (CDBI) greater than 50 percent; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one ethylene polymer characterized as having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and comprising a linear polymer fraction, as determined using a temperature rising elution fractionation (TREF) technique.

10. The film of claim 9 wherein the ethylene interpolymer (A) has a slope of strain hardening coefficient greater than or equal to 1.5.

11. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography.

12. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

13. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a single melting point, as determined using differential scanning calorimetry.

14. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and no high density polymer fraction, as determined using a temperature rising elution fractionation technique.

15. The film of claim 9 wherein the ethylene interpolymer (A) is further characterized as having a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8, as determined using gel permeation chromatography, and a single melting point as determined using differential scanning calorimetry.

16. The film of claim 9 or claim 11 wherein the ethylene interpolymer (A) is further characterized as having a no high density polymer fraction, as determined using a temperature rising elution fractionation technique, and a single melting point, as determined using differential scanning calorimetry.

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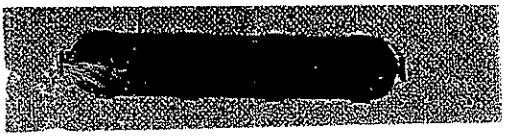

SEARCHED

Class	Sub.	Date	Exmr.
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ABOVE	UPDATED	3/31/00	RH
526	160	3/31/00	RH
526	161		
526	352		
525	142		
525	320	3/31/00	RH

INTERFERENCE SEARCHED

Class	Sub.	Date	Exmr.
525	240	4-4-00	RH
525	142	4-4-00	RH
525	320	4-4-00	RH

SEARCH NOTES

	Date	Exmr.
525/240 and linear and ethylene	3/21/00	RH
See 08/544,497	3/31/00	RH

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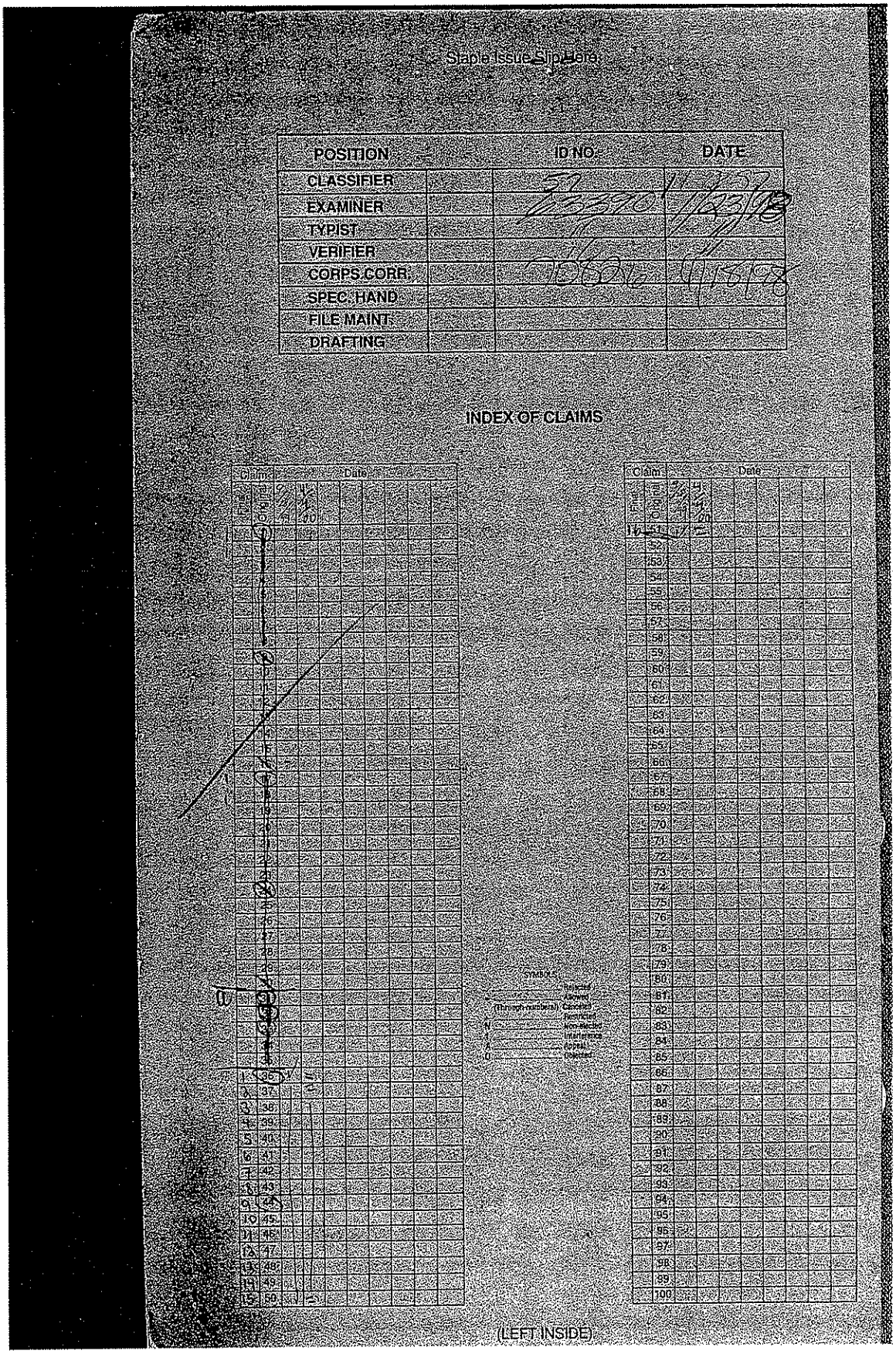
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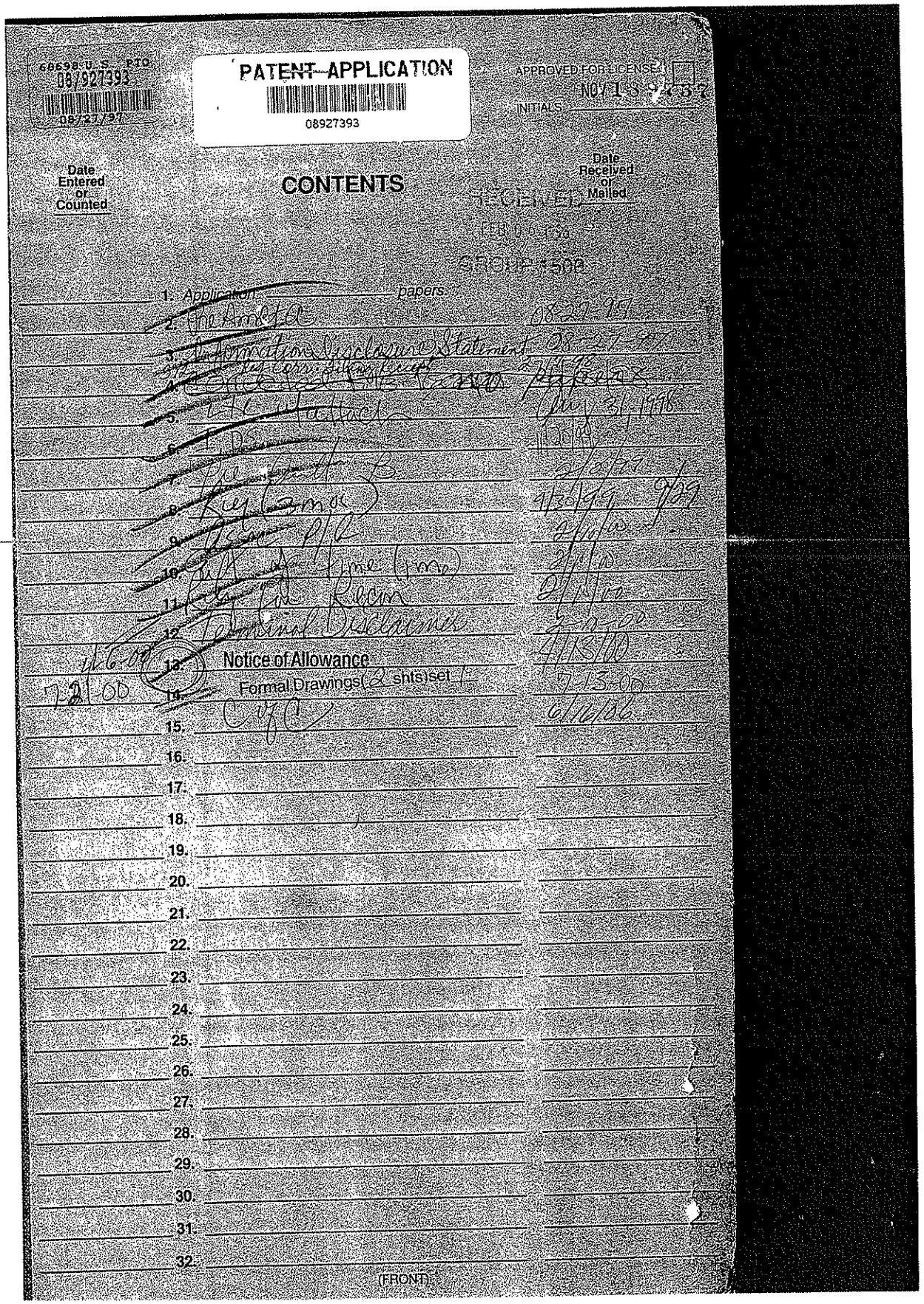

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PATENT APPLICATION
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5.	LTC Attach	July 31, 1998
6.	I.D.S.	1/20/99
7.	Pre Amt B	2/2/99
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