EXHIBIT V

PART 12

a) providing a polyolefin blend comprising at least about 30 wt.% to about 80 wt.% low M_w polyethylene having a density greater than or equal to 0.900 g/cm^3, and having a blend polydispersity index of greater than 3.5; and,

b) extruding the blend of step a) at shear rates not less than 500 s^{-1}.

8. The process according to claim 7 wherein said higher density polyethylene has a M.I. (g/10 min., 190°C, 2.16 kg) greater than or equal to 50 but less than or equal to 1000.

9. The process according to any of claims 7 - 8 wherein said polyolefin blend comprises, in addition to said polyethylene, at least one of ethylene homopolymers or copolymers wherein the ethylene content is at least 70 mol.%.

10. A polyolefin blend suitable for high shear-stress extrusion characterized by comprising :

a) from 40 wt % to not more than 80 wt.% of total polymer blend of low M_w polyethylene having a density greater than or equal to 0.900 g/cm^3; and,

b) 55 to 20 wt.% of total polymer blend of at least one of LDPE or LLDPE having density less than 0.930 wherein the ethylene content is at least 70 mol.%, preferably at least 80 mol.%, where C_3-C_{16} α-olefins and/or diolefins are copolymerized, and wherein the M.I. of the b) component is selected such that the blend of a) and b) exhibits an MWD of greater than 3.5.

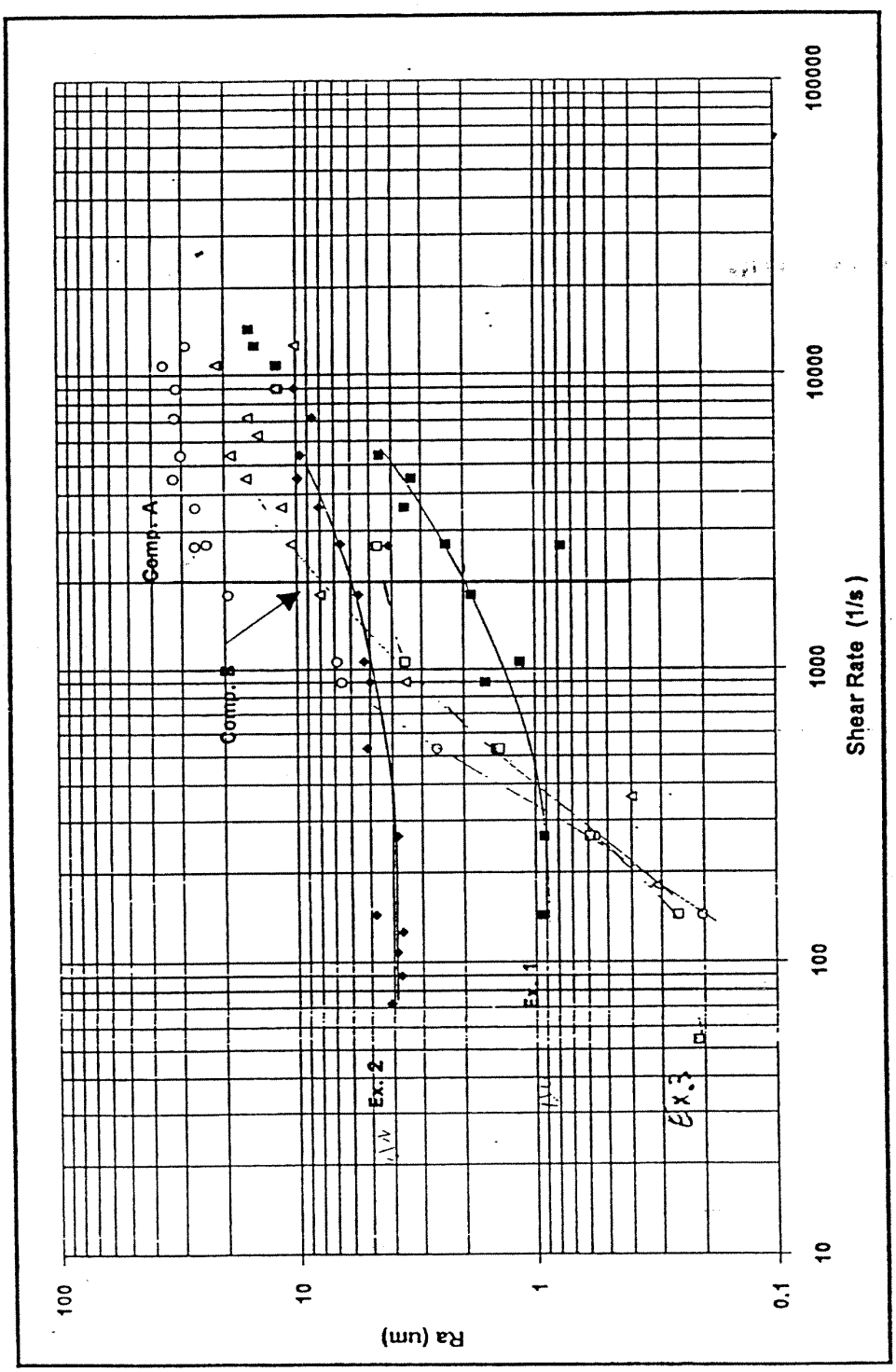

Shear Rate (1/s)
100000
10000
1000
100
10
Ra (um)
100
10
1
0.1
Comp. A
Comp. B
Ex. 1
Ex. 2
Ex. 3

FIGURE 1

INTERNATIONAL SEARCH REPORT

Int tional application No.
PCT/EP 93/03355

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08L 23/08
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A1, 9003414 (EXXON CHEMICAL PATENTS INC.), 5 April 1990 (05.04.90) -- --------	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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7 March 1994	25. 03. 94

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INTERNATIONAL SEARCH REPORT

Information on patent family members

28/01/94

International application No.
PCT/EP 93/03355

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9003414	05/04/90	AU-B- 615804	10/10/91
		AU-A- 4338089	18/04/90
		EP-A- 0389611	03/10/90
		JP-T- 3502710	20/06/91

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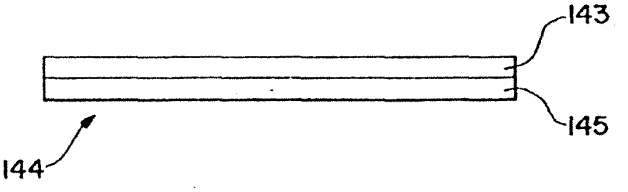
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(54) Title: *HEAT SEALABLE FILMS AND ARTICLES MADE THEREFROM*



(57) Abstract

Heat sealed articles and heat sealable films comprising a polymer blend of a first polymer having a narrow molecular weight and composition distribution and a second polymer having a broad molecular weight distribution and composition distribution. The articles and films have significantly improved physical characteristics and remarkably low heat seal initiation temperatures, high seal strength, high hot tack and therefore provide improved processibility and higher line speeds on commercial heat sealing equipment.

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HEAT SEALABLE FILMS AND ARTICLES MADE THEREFROM

FIELD OF THE INVENTION

The present invention relates to heat sealable films and articles. In particular, the invention relates to a blend of polymers one of which has a narrow molecular weight distribution and narrow composition distribution, the other has a broad molecular weight and composition distribution. The blends of the invention exhibit excellent heat sealing and other physical properties. The blends may be used to make films, bags, pouches, tubs, trays, lids, packages, containers and other articles employing a heat seal.

BACKGROUND OF THE INVENTION

Many articles of manufacture employing heat seals are currently available in the marketplace. Generally, the seals on such articles may be employed by welding two separate portions of the article together. For example, plastic parts usefully employed in machines and toys may be constructed by joining together two individual plastic pieces by heating one or both of the plastic pieces, pressing them together, and then, allowing them to cool. Specifically, heat sealing is very important in packaging applications. Packages formed by a heat seal provide for the efficient transportation of a consumer item within the package, provide a display of the consumer item that promotes sales, and, in the food industry, the packaging is employed to preserve the freshness of the consumer item. Most importantly and related to heat seal a manufacturer of packages or any other like article requiring a seal requires excellent processibility.

Various types of polymers are used to form articles, which include packages, that may be joined together or sealed by the application of heat and/or pressure. Polymers or blends of polymers used to make the articles are selected for use because they provide a strong seal, which is easily and rapidly formed by a single short application of heat and/or pressure. Occasionally, the entire heat sealed article is constructed from the same polymer or a blend of polymers or by the coextrusion of the same or different polymers.

More often, the article is constructed of various areas or layers of different materials, and polymers which provide good heat sealing properties are utilized only in areas, or layers, where heat sealing will ultimately be necessary. This type of construction is employed because the articles, for instance multilayer films, should have desirable physical and mechanical properties such as clarity, strength, resistance to puncture and tearing, in addition to heat sealing properties, and

should be easily processed by high speed equipment. Many plastic materials are known to possess good physical and mechanical properties but often do not also possess good heat sealing properties. For example, polypropylene has good strength and clarity and is resistant to tearing, but does not readily form good seals at the temperatures which are preferred in commercial sealing machinery. Conversely, some polymers with good heat sealing properties do not have adequate strength or clarity.

The packaging art has therefore developed multiple layer articles such as multilayer films incorporating one or more layers of the same or different types of polymers blended or coextruded together that provide good mechanical and physical properties and providing one or more additional layers formed from polymers that provide the article of manufacture with good heat sealing properties. In this way, for example, a film may be produced having a substrate layer of polypropylene provided for strength and clarity, and a layer of polyethylene to provide good heat sealing properties. Other articles, in addition to films, may be similarly constructed with a plurality of materials, each material selected to contribute to one or more of the desired properties of the final article.

Various types of polyethylene polymers are known in the art as having acceptable heat sealing properties. Low density polyethylene ("LDPE") is generally prepared at high pressure using free radical initiators and typically has a density in the range of 0.915-0.940 g/cm^3. LDPE is also known as "branched" polyethylene because of the relatively large number of long chain branches extending from the main polymer backbone.

High density polyethylene ("HDPE") usually has a density in the range of greater than 0.940 to 0.960 g/cm^3. HDPE is prepared using a coordination catalyst, e.g., Ziegler-Natta type catalysts, at low or moderate pressures, but sometimes at high pressure. HDPE is generally linear without any substantial side chain branching. HDPE is a substantially crystalline polymer.

Linear low density polyethylene ("LLDPE") is generally prepared in the same manner as HDPE, but incorporates a relatively minor amount of an alpha-olefin comonomer such as butene, hexene or octene to introduce enough short chain branches into the otherwise linear polymer to reduce the density of the resultant polymer into the range of that of LDPE. The coordination catalysts used to interpolymerize ethylene and the alpha-olefins generally produce a LLDPE with a broad composition distribution, as hereinafter defined, and a relatively broad molecular weight distribution, i.e., Mw/Mn greater than about 3, wherein Mw is

the weight average molecular weight and Mn is the number average molecular weight.

Polyethylenes such as LLDPE described above have a broad molecular weight distribution which can be undesirable in many respects. For example, LLDPE resins known previously in the art contain relatively high molecular weight molecules that are subject to an orientation, which results in anisotropic properties in the machine direction compared to the transverse direction of a fabrication process. The higher molecular weight molecules having low comonomer content also have less desirable heat sealing properties. On the other hand, resins containing relatively lower molecular weight molecules, in which the comonomer is invariably concentrated, have better heat sealing properties but tend to exhibit high block and tackiness properties. These lower molecular weight, highly branched molecules also interfere with the proper function of certain additives compounded in the resin, increase the percentage of extractable polymer, and increase fouling in the polymerization plant. The relatively high alpha-olefin comonomer content of these low molecular weight polymer molecules causes such polymer molecules to be generally amorphous and to exude to the surface of fabricated parts, thereby producing an undesirable sticky surface.

Previously known blends of or coextruded polyethylenes designed to improve one or more of the properties of a resulting film or the like relative to its components or relative to polyethylene homopolymers in the past have also suffered from the drawbacks mentioned above. For example, incorporating a blend component with a high average comonomer content to reduce crystallinity and improve heat sealability generally results in an increase of extractables and adversely affects other properties so that the full advantage of the blend is not realized.

Therefore, a need exists for a polymer blend that exhibits improved heat sealing while maintaining other desirable physical properties.

SUMMARY OF THE INVENTION

The blend of polymers of the invention generally include a first polymer, component A, which has a narrow molecular weight distribution and composition distribution and a second polymer, component B, which has a broad molecular weight distribution and composition distribution.

In one embodiment of the invention, component A can be produced by a metallocene catalyst as later defined in this patent specification and component B can be produced by a conventional Ziegler-Natta catalyst.

In another embodiment of the invention, component A comprises between about 40 to 99 weight percent of the total weight percent polymer blend and component B comprises between about 1 to about 60 weight percent of the total weight percent polymer blend of the invention.

In yet another embodiment, the polymer blend of the invention is useful in as a film layer in an article of manufacture, particularly in a heat sealable article where the film layer is a seal layer.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing aspects, features, and advantages of the invention will become clearer and more fully understood when the following detailed description is read in conjunction with the accompanying drawings, in which:

Figure 1 illustrates the broad molecular weight distribution and broad composition distribution of a typical prior art LLDPE.

Figure 2 illustrates the narrow molecular weight distribution and narrow composition distribution of an exemplary blend component used in the present invention.

Figure 3 is a graph of the relationship between seal strength and sealing temperature for films made from prior art polyethylene and for films made according to the invention.

Figure 4 is a graph of the relationship between seal strength and sealing temperature for films made from prior polyethylenes.

Figure 5 is a graph of the relationship between seal strength and sealing temperature for films made according to the invention compared to films made from prior art polyethylenes.

Figure 6 is a graph of the relationship between seal strength and sealing temperature for films made according to the invention in comparison to the prior art polyethylene.

Figure 7 is a graph of the relationship between seal strength and sealing temperature for films made according to the invention in comparison to the prior art polyethylene.

Figure 8 is a graph of the relationship between seal strength and sealing temperature for films according to the invention compared to a prior art polyethylene.

Figure 8A is a graph illustrating the seal initiation temperature and plateau on-set temperatures for the inventive blends in comparison to prior art polyethylene.

Figure 9 is a cross-sectional view of a sealed container according to the invention.

Figure 10 is a cross-sectional view of a film, or lid or sealing member to the invention.

DETAILED DESCRIPTION OF THE INVENTION

Introduction

The invention concerns a blend of a metallocene catalyzed polymer, component A and a conventional Ziegler-Natta catalyzed polymer, component B, their production and applications for their use. The polymer blend of the invention has unique properties which make them particularly well suited for use in polymeric films. These films are very useful in applications requiring heat sealability.

It has been discovered previously that polymers derived from metallocene catalyst systems surprisingly heat seal extremely well, as compared to polymer produced by conventional Ziegler-Natta catalysts, see PCT Application No. WO 93/03093, published February 18, 1993. However, these polymers do not process as well as polymers produced with a conventional catalyst. Typically, to improve processability blends of polymers are formed as previously discussed. These blends generally possess some of the better properties each polymer has individually with an increase in other undesirable properties. Also, the better properties of each polymer are greatly reduced when blended.

Surprisingly and unexpectedly applicants have discovered a polymer blend that retains improved heat sealing and improved processability while maintaining other desirable physical properties.

Production of Polymer Component A of the Invention

The polymer, component A, of this invention can be produced using metallocene catalyst systems in a polymerization or copolymerization process in gas, slurry solution or high pressure phase.

The process for polymerizing or copolymerizing involves the polymerization of one more of the alpha-olefin monomers having from 2 to 20 carbon atoms, preferably 2-15 carbon atoms. The invention is particularly well suited to the copolymerization reactions involving the polymerization of one or more of the monomers, for example alpha-olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1 and cyclic olefins such as styrene. Other monomers can include polar vinyl, dienes, norbornene, acetylene and aldehyde monomers. Preferably a copolymer of

ethylene is produced such that the amount of ethylene and comonomer is adjusted to produce a desired polymer product. Preferably the comonomer is an alpha-olefin having from 3 to 15 carbon atoms, more preferably 4 to 12 carbon atoms and most preferably 4 to 10 carbon atoms. In another embodiment ethylene is polymerized with at least two comonomers to form a terpolymer and the like. If a comonomer is used then the monomer is generally polymerized in a proportion of 70.0-99.99, preferably 70-90 and more preferably 80-95 or 90-95 mole percent of monomer with 0.01-30, preferably 3-30 and most preferably 5-20, 5-10 mole percent comonomer.

For the purposes of this patent specification the term "metallocene" is defined to contain one or more cyclopentadienyl moiety in combination with a transition metal. The metallocene catalyst component is represented by the general formula $(C_p)_mMR_nR'_p$ wherein C_p is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IV, V or VI transition metal; R and R' are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; m=1-3, n=0-3, p=0-3, and the sum of m+n+p equals the oxidation state of M. The metallocene can be substituted with principally hydrocarbyl substituent(s) but not to exclude a germanium, a phosphorous, a silicon or a nitrogen atom containing radical or unsubstituted, bridged or unbridged or any combination.

Various forms of the catalyst system of the metallocene type may be used in the polymerization process of this invention. Exemplary of the development of these metallocene catalysts for the polymerization of ethylene is found in U.S. Patent No. 4,871,705 to Hoel, U.S. Patent No. 4,937,299 to Ewen, et al. and EP-A-0 129 368 published July 26, 1989, and U.S. Patent Nos. 5,017,714 and 5,120,867 to Welborn, Jr. all of which are fully incorporated herein by reference. These publications teach the structure of the metallocene catalysts and includes alumoxane as the cocatalyst. There are a variety of methods for preparing alumoxane one of which is described in U.S. Patent 4,665,208.

Other cocatalysts may be used with metallocenes, such as trialkylaluminum compounds; or ionizing ionic activators or compounds such as, tri (n-butyl) ammonium tetra (pentaflurophenyl) boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing ionic compound. Such compounds are described in EP-A-0 520 732, EP-A-0 277 003 and EP-A-0 277 004 both published August 3,

1988 and U.S. Patent Nos. 5,153,151 and 5,198,401 and are all herein fully incorporated by reference.

Further, the metallocene catalyst component can be a monocyclopentadienyl heteroatom containing compound. This heteroatom is activated by either an alumoxane or an ionic activator to form an active polymerization catalyst system to produce polymers useful in this present invention. These types of catalyst systems are described in, for example, PCT International Publications WO 92/00333 published January 9, 1992, U.S. Patent Nos. 5,096,867 and 5,055,438, EP-A-0 420 436 and WO 91/ 04257 all of which are fully incorporated herein by reference.

In addition, the metallocene catalysts useful in this invention can include non-cyclopentadienyl catalyst components, or ancillary ligands such as boroles or carbollides in combination with a transition metal. Additionally it is not beyond the scope of this invention that the catalysts and catalyst systems may be those described in U.S. Patent No. 5,064,802 and PCT publications WO 93/08221 and WO 93/08199 published April 29, 1993 all of which are herein incorporated by reference. All the catalyst systems described above may be, optionally, prepolymerized or used in conjunction with an additive or scavenging component to enhance catalytic productivity.

The catalyst particles in a gas phase process may be supported on a suitable particulate material such as polymeric supports or inorganic oxide such as silica, alumina or both. Methods of supporting the catalyst of this invention are described in U.S. Patent Nos. 4,808,561, 4,897,455, 4,937,301, 4,937,217, 4,912,075, 5,008,228, 5,086,025, 5,147,949, 5,238,892 and 5,240,894, all of which are herein incorporated by reference.

Characteristics of Polymer Component A of the Invention

A key characteristic of polymer Component A of the present invention is its composition distribution (CD). As is well known to those skilled in the art, the composition distribution of a copolymer relates to the uniformity of distribution of comonomer among the molecules of the copolymer. Metallocene catalysts are known to incorporate comonomer very evenly among the polymer molecules they produce. Thus, copolymers produced from a catalyst system having a single metallocene component have a very narrow composition distribution - most of the polymer molecules will have roughly the same comonomer content, and within each molecule the comonomer will be randomly distributed. Ziegler-Natta catalysts, on the other hand generally yield copolymers having a considerably

broader composition distribution. Comonomer inclusion will vary widely among the polymer molecules.

A measure of composition distribution is the "Composition Distribution Breadth Index" ("CDBI"). CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50% (that is, 25% on each side) of the median total molar comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is Temperature Rising Elution Fraction (TREF), as described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, which are incorporated herein by reference.

To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from the TREF technique described above. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature the weight fractions less than 15,000 are ignored. These low weight fractions generally represent a trivial portion of the resin of the present invention. The remainder of this description and the appended claims maintain this convention of ignoring weight fractions below 15,000 in the CDBI measurement.

From the weight fraction versus composition distribution curve the CDBI is determined by establishing what weight percent of the sample has a comonomer content within 25% each side of the median comonomer content. Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993.

The polymers of the present invention have CDBI's generally in the range of 50-98%, usually in the range of 60-98% and most typically in the range of 65-95%. Obviously, higher or lower CDBI's may be obtained using other catalyst systems with changes in the operating conditions of the process employed.

MWD, or polydispersity, is a well known characteristic of polymers. MWD is generally described as the ratio of the weight average molecular weight (Mw) to the number average molecular weight (Mn). The ratio Mw/Mn can be measured directly by gel permeation chromatography techniques.

Those skilled in the art will appreciate that there are several methods for determining MWD of a polymer sample. For the purposes of this patent specification the molecular weight distribution of a polymer can be determined with a Waters Gel Permeation Chromatograph equipped with Ultrastyrogel columns and a refractive index detector. In this development, the operating temperature of the instrument was set at 145°C, the eluting solvent was trichlorobenzene, and the calibration standards included sixteen polystyrenes of precisely known molecular weight, ranging from a molecular weight of 500 to a molecular weight of 5.2 million, and a polyethylene standard, NBS 1475.

The MWD of the polymer component A of this invention are termed "narrow". For the purposes of this patent specification "narrow" MWD means a Mw/Mn less than about 3, preferably less than or equal to 2.5.

The MI of the polymers of the invention are generally in the range of about 0.1 dg/min to about 1000 dg/min, preferably about 0.2 dg/min to about 300 dg/min, more preferably about 0.3 to about 200 dg/min and most preferably about 0.5 dg/min to about 100 dg/min.

Contemplated densities of component A of the invention are in the range of 0.85 to 0.96 g/cm^3, preferably 0.87 to 0.940 g/cm^3, more preferably 0.88 to about 0.935 g/cm^3. In another embodiment the density of component A is in the range of 0.900 to 0.915 g/cm^3, 0.915 to 0.940 g/cm^3, 0.88 to 0.9 g/cm^3 and greater than 0.940 g/cm^3 to 0.96 g/cm^3.

In another embodiment, component A can comprise a blend of component A polymers, which can be prepared by blending the desired components in the desired proportion using conventional blending techniques and apparatus, such as, for example, screw-type extruders, Banbury mixers, and the like. Alternatively, the blends may be made by direct polymerization, without isolation of the blend components, using, for example, two or more catalysts in one reactor, or by using a single catalyst and two or more reactors in series or parallel.

Characteristics of Polymer Component B of the Invention

Polymer, component B, of the invention is very well known in the art and may be prepared by a traditional Ziegler-Natta catalysis. For example, U.S. Patent No. 4,719,193, incorporated herein by reference, discloses a method of preparing traditional polyethylene copolymers. Other references include U.S. Patent No. 4,438,238, V.B.F. Mathot and M.F.J. Pijpers, J. Appl. Polym. Sci., 39, 979 (1990), and S. Hosoda, Polymer Journal, 20, 383 (1988).

Generally, the molecular weight of the B component copolymer is in the range of 40,000 to 300,000, the melt index (MI) should be 0.05 to 20 and the density ranges from 0.9 to 0.95 g/cm^3. The amount of comonomer polymerized with ethylene ranges from 0.5 to 5 mole percent and the density ranges from 0.91 to 0.93 g/cm^3. Comonomers listed above for preparing A component polymers are useful as well in forming B component polymers. Hydrogen may be utilized, as is well-known, to adjust the molecular weight of the resulting polymers. Typically polymer component B have a molecular weight distribution greater than 3.5 more desirably greater than 4.0.

The B component of the polymer blend of the invention may consist of a blend of different prior art polymers, each differing in one or more of: molecular weight, MWD, comonomer type and content, density, MI and CD.

BLENDS, FILMS AND ARTICLES OF THE INVENTION

The polymer blend of the invention, herein referred to as, the "A-B blend", may be used to form articles with particularly desirable heat sealing properties. In particular, the A-B blend may be processed into films which possess particularly desirable heat sealing characteristics.

For example, the A-B blend may be used to form films which are in turn formed into bags or pouches by heat sealing techniques known in the art. The heat sealable film may also be used as package sealing material, for example, the film may be placed over the opening of a container, and then secured to the container by the application of heat. This technique may be used to seal perishable items, such as food, into paper, plastic, glass, ceramic or metallic containers. The technique may also be used to package consumer items in attractive sales displays and to secure items for transportation.

The articles described herein are formed from the A-B blend of the invention. The articles may comprise other materials, especially in portions of the article not be utilized for heat sealing. In the portions of the article that are used for heat sealing, the language "formed from" is intended to mean "comprising." In one embodiment, all articles or portions of articles described herein may also be constructed to consist essentially of the inventive A-B blends. In other words, the heat sealing portion of any article described herein may consist essentially of the inventive A-B blend or of the polymer.

The A-B blend of polymers may be formed into films by methods well known in the art. For example, the polymers may be extruded in a molten state through a flat die and then cooled. Alternatively, the polymers may be extruded in

cost savings associated with operating a process with significantly lower temperatures.

EXAMPLES

In order to provide a better understanding of the present invention the following examples are offered as related to actual tests performed in the practice of this invention, and illustrate the surprising and unexpected properties of the A-B blends of the invention and are not intended as a limitation on the scope of the invention.

EXAMPLE I

An ethylene copolymer resin was prepared according to the prior art and is identified as Sample No. U3. Sample U3 was prepared in a fluidized bed gas phase reactor employing a titanium metal catalyst as described below. The prior art transition metal catalyst was prepared in accordance with procedures outlined in U. S. Patent 4,719,193 which is incorporated herein by reference. Silica was calcined at 600°C and then treated with triethylaluminum in a mixture of isopentane at 25°C. Magnesium dichloride was then reacted with titanium trichloride in the presence of aluminum trichloride and tetrahydrofuran (THF) solvent at 60°C. The resulting reaction product was contacted in THF solvent at 50°C with the treated silica prepared as noted above. The resulting product was treated with a mixture of diethylaluminum chloride and tri-n-Hexyl aluminum in isopentane at 50°C to yield the catalyst used to prepare Sample U3. The gas phase reaction was carried out at 83°C reaction temperature, an ethylene pressure of 130 psia, hydrogen/ethylene mole ratio of 0.0556, a butene/ethylene ratio of 0.0263 and a residence time of 2.4 hours. The melt index of the copolymer as determined by ASTM-1238 was approximately 1.0 g/10 min, and a density of 0.918 g/cc. Example U5, was done similar to example U3. Examples U1, U2, U4, U6, and U8 were also carried out similar to example U3, except the comonomer was changed from butene to hexene.

EXAMPLE II

Sample No. U2 is prepared using traditional Ziegler Natta catalyst systems and in isopar solvent, reaction temperature of 150-220°C, pressure of 400-600 psig, and octene/ethylene mole ratio of approximately 2.3.

EXAMPLE III

Sample No. U7 is prepared using a catalyst system of titanium tetrachloride and diethyl aluminum chloride, in a series slurry reactors. In the first reactor the

ethylene is polymerized to give relatively low molecular weight polymer, and in the second reactor butene comonomer is used and molecular weight is increased.

EXAMPLE IV

Sample No. U9, is prepared using free radical initiation of ethylene under high pressure conditions in a tubular reactor. The reactor temperature range is 149-260°C, and pressure range of 36,000 to 45,000 psig and a residence time of 2 sec to 30 sec.

EXAMPLE V

A silica supported transition metal catalyst was used for preparation of Sample X1. The supported catalyst preparation is described below. About 100 grams of high surface area (Davison 952) silica, was dehydrated by heating the silica to 800°C for about 5 hours and maintaining flow of dry nitrogen over the silica. The dry silica was then slurried with 500 ml of dry toluene at 25°C under a nitrogen atmosphere in a 2500 ml round-bottom flask equipped with a magnetic stirrer. Thereafter, 250 ml of methyl alumoxane in toluene (1.03 moles/liter in aluminum) was added dropwise over about 15 minutes with constant stirring of the silica slurry. Stirring was subsequently continued for 30 minutes while maintaining the temperature of the flask at 25°C. A toluene solution containing 2.00 grams of bis(n-butylcyclopentadienyl)zirconium dichloride was added to the alumoxane treated silica slurry dropwise over 15 minutes. Stirring was maintained constantly during the addition and for one additional half hour while maintaining the temperature of the slurry at 65°C. Thereafter, toluene was decanted and the solids were recovered and dried under a vacuum for four hours. Analysis of the catalyst indicated that it contained 4.5 wt% aluminum and 0.63 wt% zirconium.

Sample No. X1 was prepared using the catalyst mentioned above, under gas phase conditions, reaction temperature of 63°C, hydrogen concentration of 475 ppm, ethylene/butene mole ratio of 41.5/5.17.

EXAMPLE VI

Sample No. X3, is prepared using silicon bridged transition metal catalyst. The catalyst preparation is outlined in U. S. Patents 5,017,714 and 5,120,867, incorporated herein by reference. Sample No. X3 is prepared using the catalyst mentioned above, and reaction conditions of pressure 19000 psig, temperature 131°C, butene 66 mole%, and butene/ethylene mole ratio of 1.9. Samples, X2, X4, and X5 are also prepared using similar conditions used for Sample No. X3.

The polymer properties and the catalyst and process details on the polymers described in Examples 1-6 are shown in Table I.

EXAMPLE VII

The films numbered EX. 1, 8-10, 13,14,17,20,23,28, and 35 were made on a 1 inch Killion Mini Cast Line, Model KLB 100, having thickness of 1.5 to 2.0 mils (37.5 to 50 microns).

The blends of samples numbered EX. 2-7, CEX. 1-2, EX. 11,12,15,16,18,19,21,22,24-27, and 29-37 (except EX. 35) were melt homogenized on a Werner Pfleiderer Model ZSK-57 twin screw extruder and pelletized. The blends were converted into films having a thickness of 1.5 to 2.0 mils (37.5 to 50 microns) using a 1 inch Killion Mini Cast Line, Model KLB 100.

The blend samples numbered EX. 39-44 were dry blended, followed by blown film extrusion on a 1 1/2 inch Egan Line (Tower Flight Model) using 4/1 blowup ratio. The film thickness was approximately 2.0 - 2.3 mils (50 - 58 microns).

Heat seals were made from the films on a laboratory scale Theller Model EB heat sealer. A dwell time of about one second and a sealing pressure of 50 N/cm^2 was used for making the seals. The seals on the films were made in the transverse direction for both blown and cast films and the heat sealing anvils were insulated from the heat sealing film by a Mylar® film. The Mylar® film is very stable at normal heat sealing temperatures and is easily removed from the heat sealing polymer after the seal has been made. The seals were aged for 24 hours before testing them for strength.

For the strength test, the sealed samples were cut into 0.5 inch (1.27 cm) wide pieces and then strength tested using an Instron instrument at a crosshead speed of 20 inches/min (508 mm/min) and a 2 inch (5.08 cm) jaw separation. The free ends of the samples are fixed in the jaws, and then the jaws are separated at the strain rate until the seal fails. The peak load at the seal break is measured and the seal strength is calculated by diving the peak load by the sample width. The seal strength values for all the films were normalized for a film thickness of 2.0 mils.

The heat seal initiation temperature was determined by measuring the seal strengths of each sample sealed at various temperatures and then extrapolating from a plot of seal strength versus temperature to find the lowest temperature at which some seal strength is present. This same plot can be used to determine the temperature at which a seal strength of 2 N/cm occurs. The plot can also be used to determine the plateau on-set temperature which is defined as the temperature at

which the seal strength remains relatively constant. In addition, the plateau on-set temperature represents the temperature at which tearing failure mode occurs.

The seal strength values determined on film samples numbered EX. 1-9, CEX. 1,2 and heat sealed at different temperatures are shown in Table II. The seal initiation temperatures, and plateau on-set temperatures for the film samples numbered EX. 1-9, and CEX. 1,2 are also shown in Table II.

The seal strength values determined on film samples numbered EX. 10-27 and heat sealed at different temperatures are shown in Table III. The seal initiation temperatures, and plateau on-set temperatures for the film samples numbered EX. 10-27 are also shown in Table III.

The seal strength values determined on film samples numbered EX. 10, 14, and 28-38, and heat sealed at different temperatures are shown in Table IV. The seal initiation temperatures, and plateau on-set temperatures for the film samples numbered EX. 10, 14, and 28-38, are also shown in Table IV.

The seal strength values determined on film samples numbered EX. 14, and 39-44, and heat sealed at different temperatures are shown in Table V. The seal initiation temperatures, and plateau on-set temperatures for the film samples numbered EX. 14, and 39-44, are also shown in Table V.

Figure 3 represents the seal strength versus temperature curves for samples numbered EX. 1-4 and 8 (Table II). The curve for the inventive sample EX. 4 shows seal initiation temperature approaching that of the film made from the narrow CD and MWD polymer sample EX. 8. In comparison to the prior art sample EX. 1, the seal initiation and plateau on-set temperatures for EX. 4 are unexpectedly lower and this improves the productivity during the sealing. A seal strength of 4 N/cm for the inventive blend samples numbered EX. 2, EX.3, and EX.4 are approximately 108, 103, and 95°C respectively, in comparison to 113°C for the prior art sample numbered EX. 1. Importantly, the plateau on-set temperature EX.4 and EX. 5 is lowered by 10° and 20°C respectively (Table II) in comparison to the prior art sample EX. 1.

Figure 4 represents the seal strength versus temperature curves for samples numbered EX.1 and 9, and for comparative blend samples CEX.1, and 2 (Table II). The comparative blends CEX.1 and 2 are made from two resins which are broad in CD and MWD and having the same density difference between EX.1 and EX. 8. Even though there is some improvement in the seal initiation temperature for the samples CEX.1 and 2, the plateau on-set temperature remains unaffected in comparison to EX. 1.

Figure 5 represents the seal strength versus temperature curves for the inventive samples numbered EX. 4 and 5 versus CEX.2. The seal initiation temperature for the inventive blends is considerably lower and also the plateau on-set temperature is lowered by 10-20°C in comparison to CEX.2, while the plateau seal strength for all the samples remains almost constant.

Figure 6 represents the seal strength versus temperature curves for the inventive samples numbered EX.33 and 34 in comparison to the prior art sample EX.14 (data shown in Table IV). As is evident the seal initiation temperature is lowered significantly in comparison to the prior art sample EX.14, in addition to the lowering of plateau on-set temperature (Table IV). Another unexpected observation with the inventive blend samples EX. 33 and 34 is the higher plateau seal strength versus the prior art sample EX. 14.

Figure 7 represents the seal strength versus temperature curves for the inventive blend samples numbered EX. 36 and 37 in comparison to the prior art sample numbered EX.35 (data shown in Table IV). As is demonstrated earlier the seal initiation temperature for the inventive samples are significantly lower and the plateau seal strength remains fairly high and almost equivalent to the prior art sample EX.35.

Figure 8 represents the seal strength versus temperature curves for the inventive blend samples numbered EX. 39-41 in comparison to the prior art sample EX. 14 (data shown in Table V). These inventive blend samples EX. 39-41 which were made by dry blending the two individual resins and made into films show the unexpected and significantly lower seal initiation temperature in comparison to the prior art sample EX. 14. Another unexpected observation with the inventive blend samples EX. 39-41 is the peeling failure mode of the seals during testing, where the two sealed surfaces are cleanly separated even for samples sealed at high temperature. More importantly, the sealing window, which is defined as the temperature range in which the seal strength remains high and constant is very broad for the inventive blends EX. 39-41. The sealing window for the inventive blend samples EX. 39-41 extends over a broad temperature range of 65-160°C, while the sealing window for the prior art sample EX. 14 was only from 120-160°C. The same peelable failure mode behavior was also observed for inventive blend samples numbered EX. 42-44 (data shown in Table V).

Figure 8A represents the relationship between observed seal initiation temperature and observed plateau on-set temperature versus composition for the inventive blends (EX. 2-7) in comparison to the prior art polyethylene (EX.1) and

the polyethylene having narrow CD and MWD (EX.8) (data is shown in Table 2). Also in Figure 8A, the expected seal initiation temperature and the expected plateau on-set temperatures for the inventive blends over the entire composition is presented. The inventive blends clearly show the unexpected improvement in the seal initiation temperature and plateau on-set temperature.

All the inventive blend samples shown in Table II, III, IV, and V, except samples numbered EX. 24-27 (except EX. 19, Table III), having compositions of 60/40 and 40/60 (broad CD resins/narrow CD resins) give a seal strength level ≥ 3 N/cm for seals made at 95°C, and higher than 5 N/cm seal strength for seals made at 100°C. In comparison, seal strength levels of 3 and 5 N/cm for the prior art samples numbered EX. 1, 9, 10, 14, 17, 20, 23, 28, 35, and CEX. 2 are not obtained unless the seal temperatures are 110°C and above.

The commercial advantages to be obtained through the use of the inventive type of heat sealing articles is apparent from the figures. The inventive articles may be adequately sealed at temperatures of less than 120°C, 110°C, or 100°C, and yet retain adequate strength in the seal thus formed. In comparison prior art polymers sealed at 100°C, 110°C, or even at 120°C and higher may not yield seals of substantial strength. It is therefore possible to use the inventive materials in commercial lines operating at a sealing temperature as low as 100°C or less. An operating temperature of 100°C is substantially lower than normal commercial sealing operating temperatures. With sealing temperatures as low as 100°C, substantial increases in heat sealing speed may be achieved and therefore the output of a heat sealing unit may be remarkably increased by the use of the inventive heat sealing materials.

While the present invention has been described and illustrated by reference to particular embodiments thereof, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. For instance, the catalyst system may comprise various other transition metal metallocenes that are activated by alumoxane and/or ionic activators as the cocatalyst to produce polymers having a narrow molecular weight distribution and narrow composition distribution. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

TABLE I

SAMPLE ID	DENSITY (g/cc)/ MI (g/10 min)	CDBI %	PROCESS/CATALYST
EH. Copolymer (U1)	0.925/1.0	-	Gas Phase
EO Copolymer (U2)	0.905/5.0	46	Solution
EB Copolymer (U3)	0.918/1.0	38	Gas Phase
EH Copolymer (U4)	0.917/1.0	34.3	Gas Phase
EB Copolymer (U5)	0.925/1.5	-	Gas Phase
EH Copolymer (U6)	0.935/1.0	-	Gas Phase
E Homopolymer (U7)	0.952/0.05	-	Series Slurry/$TiCl_4$ & DEAC
EH Copolymer (U8)	0.925/0.8	-	Gas Phase
HP-LDPE (U9)	0.925/2.0	-	Tubular/Free Radical/High Pressure
EB Copolymer (X1)	0.905/5.0	66	Gas Phase
EB Copolymer (X2)	0.905/4.5	91.6	High Pressure
EB Copolymer (X3)	0.887/4.5	93	High Pressure
EH Copolymer (X4)	0.885/4.0	91.9	High Pressure
EB Copolymer (X5)	0.878/3.0	-	High Pressure

TABLE II
Example (EX) or Comparative Examples (CEX)

	U1	X1	SIT	POT	Strength of Seal Part (N/cm)						
	0.925 (g/cc)	0.905 (g/cc)	(°C)	(°C)	90°C	95°C	100°C	110°C	120°C	130°C	140°C
EX.1	100	0	111	130	-	0.22	0.36	1.76	9.2	9.96	9.77
EX.2	90	10	107	125	-	0.21	0.40	6.88	9.3	9.8	9.83
EX.3	80	20	100	120	-	0.16	1.18	7.26	9.64	9.14	9.05
EX.4	60	40	90	120	0.61	4.19	6.16	7.6	8.82	8.88	8.84
EX.5	40	60	85	110	1.23	3.89	5.38	8.04	8.46	8.66	7.87
EX.6	20	80	85	110	1.8	4.41	6.11	7.64	7.86	7.24	7.13
EX.7	10	90	85	110	1.89	4.23	5.4	7.07	7.14	6.9	7.0
EX.8	0	100	85	110	2.25	4.22	5.86	6.95	7.1	6.8	6.22
	U1	U2									
	0.925 (g/cc)	0.905 (g/cc)									
CEX.1	80	20	105	130	-	0.22	0.32	5.6	8.3	8.99	8.49
CEX.2	60	40	101	130	0.23	0.22	0.79	7.08	8.17	8.67	8.6
EX.9	0	100	97	130	-	0.30	1.28	5.2	6.0	6.38	6.21

SIT - Seal Initiation Temperature
POT - Plateau Onset Temperature Representing the Tearing Failure Mode

TABLE III
Example (EX) or Comparative Examples (CEX)

	U3	X2	SIT	POT	Strength of Seal Part (N/cm)						
	0.918 (g/cc)	0.905 (g/cc)	(°C)	(°C)	90°C	95°C	100°C	110°C	120°C	130°C	140°C
EX.10	100	0	98	125	0.13	0.22	0.68	7.24	8.38	8.13	8.9
EX.11	80	20	95	125	0.06	0.37	3.7	5.85	6.73	6.94	6.76
EX.12	60	40	87	120	1.9	4.57	5.41	6.43	7.19	7.57	7.14
EX.13	0	100	77	102	3.6	4.92	6.08	6.69	6.46	6.3	6.33
	U4	X2									
	0.917 (g/cc)	0.905 (g/cc)									
EX.14	100	0	102	130	0.12	0.15	0.37	6.96	8.36	8.86	8.9
EX.15	80	20	102	130	0.20	0.26	0.41	6.74	7.78	8.31	8.13
EX.16	60	40	90	125	0.38	3.02	5.45	6.29	7.64	7.91	7.21
	U5	X2									
	0.925 (g/cc)	0.905 (g/cc)									
EX.17	100	0	117	130	-	0.04	0.05	0.16	7.87	8.42	8.69
EX.18	80	20	105	125	-	0.11	0.21	4.09	7.89	8.72	8.28
EX.19	60	40	95	125	0.14	0.38	4.92	6.37	7.47	8.04	7.4

	U6	X2	SIT	POT	Strength of Seal Part (N/cm)							
	0.935 (g/cc)	0.905 (g/cc)	(°C)	(°C)	90°C	95°C	100°C	110°C	120°C	130°C	140°C	
EX.20	100	0	115	130	-	-	-	0.19	3.59	11.23	10.95	
EX.21	80	20	114	130	-	-	-	0.29	8.59	9.31	9.52	
EX.22	60	40	110	130	-	-	-	0.69	7.37	8.62	8.59	
	U7	X1										
	0.952 (g/cc)	0.905 (g/cc)	(°C)	(°C)	90°C	95°C	100°C	110°C	120°C	130°C	140°C	150°C
EX.23	100	0	126	137	-	-	-	-	0.05	2.6	20.2	29.16
EX.24	80	20	125	135	-	-	-	-	0.24	2.59	19.43	24.07
EX.25	60	40	121	135	-	-	-	0.07	0.41	4.41	16.35	19.2
EX.26	40	60	102	135	0.14	0.22	0.44	1.7	9.63	12.3	13.03	13.02
EX.27	20	80	85	125	3.01	4.98	6.84	9.08	10.54	11.0	10.76	10.72
EX.28	0	100	85	110	2.25	4.22	5.86	6.95	7.1	6.8	6.22	6.4

SIT - Seal Initiation Temperature
POT - Plateau Onset Temperature Representing the Tearing Failure Mode

TABLE IV
Example (EX) or Comparative Examples (CEX)

	U8	X3	SIT	POT	Strength of Seal Part (N/cm)						
	0.925 (g/cc)	0.887 (g/cc)	(°C)	(°C)	80°C	90°C	95°C	100°C	110°C	120°C	130°C	140°C
EX.28	100	0	102	130	-	0.16	0.24	0.43	5.62	8.46	9.4	8.93
EX.29	80	20	87	120	0.22	0.64	1.14	3.52	8.72	10.27	10.71	10.56
EX.30	60	40	85	125	0.23	3.15	5.7	6.85	8.17	9.55	10.32	9.6
	U3	X3										
	0.918 (g/cc)	0.887 (g/cc)										
EX.10	100	0	98	125	-	0.13	0.22	0.68	7.24	8.38	8.86	7.93
EX.31	80	20	90	120	-	0.41	3.16	5.61	7.01	7.79	7.99	8.35
EX.32	60	40	73	110	2.83	5.0	5.67	6.55	9.05	9.26	8.54	8.03
	U4	X3										
	0.917 (g/cc)	0.887 (g/cc)										
EX.14	100	0	102	130	-	0.12	0.15	0.37	6.96	8.36	8.86	8.9
EX.33	80	20	85	120	0.28	1.86	3.76	6.61	8.71	10.96	10.96	9.43
EX.34	60	40	75	125	1.45	5.09	5.61	6.31	8.06	9.48	9.38	8.89
	U9	X3										
	0.925 (g/cc)	0.887 (g/cc)										
EX.35	100	0	108	110	-	0.09	0.14	0.26	5.9	7.49	9.58	9.46
EX.36	80	20	95	115	-	0.24	0.43	3.37	9.25	9.62	9.14	9.49
EX.37	60	40	83	117	0.13	2.9	4.44	6.57	8.03	8.07	8.12	8.15
EX.38	0	100	55	80	4.34	4.59	4.32	4.09	4.35	4.32	4.17	-

SIT - Seal Initiation Temperature
POT - Plateau Onset Temperature Representing the Tearing Failure Mode

* All the Blends up to EX.38 were made by melt blending (melt homogenization), followed by cast film extrusion

TABLE V
Example (EX) or Comparative Examples (CEX)

	U4	X4	SIT	POT	Strength of Seal Part (N/cm)								
	0.917 (g/cc)	0.885 (g/cc)	(°C)	(°C)	70°C	80°C	90°C	95°C	100°C	110°C	120°C	130°C	140°C
EX.14	100	0	102	130	-	-	0.12	0.15	0.37	6.96	8.36	8.86	8.9
EX.39	80	20	97	130	-	-	-	0.33	0.69	5.28	6.36	7.19	7.37
EX.40	70	30	70	127	0.49	4.39	5.4	5.49	6.08	6.15	6.11	6.84	6.55
EX.41	60	40	62	125	1.88	5.2	5.32	5.53	5.47	5.42	5.58	6.53	5.71
	U4	X5											
	0.917 (g/cc)	0.878 (g/cc)											
EX.42	80	20	65	130	1.97	4.59	5.24	5.34	6.66	6.6	6.38	6.96	6.67
EX.43	70	30	60	130	3.72	5.34	5.23	5.4	5.33	5.23	5.53	5.67	5.85
EX.44	60	40	55	127	3.16	4.47	4.52	4.48	4.48	4.6	4.75	5.02	4.97

SIT - Seal Initiation Temperature
POT - Plateau Onset Temperature Representing the Tearing Failure Mode

The Seal Strength Data Reported is for an Average Film Thickness of 2.0 - 2.3 mils. For Films Having Higher Thickness, the Seal Strength Data is Normalized for 2.0 mils.

* Samples EX.39 to EX.44 were made by dry-blending the two components, followed by blown film extrusion.

CLAIMS

We Claim:

1. A polymer blend comprising from 40 to 99 weight percent of a first component comprising at least one first polymer having a molecular weight distribution less than 3 and/or a composition distribution breadth index greater than 50 percent and from 1 to 60 weight percent of a second component comprising at least one second polymer having a molecular weight distribution greater than 3 and a composition distribution breadth index less than 50 percent.

2. The polymer blend of claim 1 wherein the first polymer has a composition distribution breadth index greater than 60%, preferably greater than 70%.

3. The polymer blend of claim 1 wherein said polymer blend comprises from 60 to 99 weight percent of said first component, and preferably 60 to 90 weight percent.

4. The polymer blend of any preceding claim wherein said first polymer has a density in the range of about 0.875 g/cm^3 to about 0.96 g/cm^3, preferably 0.88 g/cm^3 to 0.94 g/cc..

5. The polymer blend of any preceding claim wherein said first polymer is an ethylene interpolymer.

6. The polymer blend of any preceding claim wherein said second polymer is LLDPE or a blend of a LLDPE with one of the group consisting of LDPE, HDPE, PP or the like.

7. A film comprising the polymer blend of any preceding claim.

8. The film of claim 7 wherein said film when used as a seal layer has a seal initiation temperature less than 100°C and/or a plateau-on-set temperature less than 120°C.

9. The film of claims 7 and 8 wherein said film at a sealing temperature of about 95°C has a seal strength at room temperature greater than about 3 N/cm,

and/or a sealing temperature of about 100°C has a seal strength at room temperature greater than about 5 N/cm.

10. A heat sealable film comprising the polymer blend of claims 1-6.

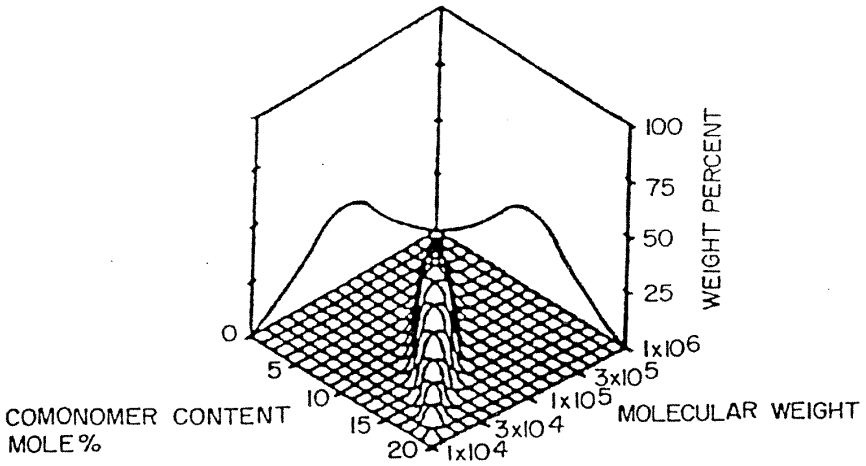


FIG. 1

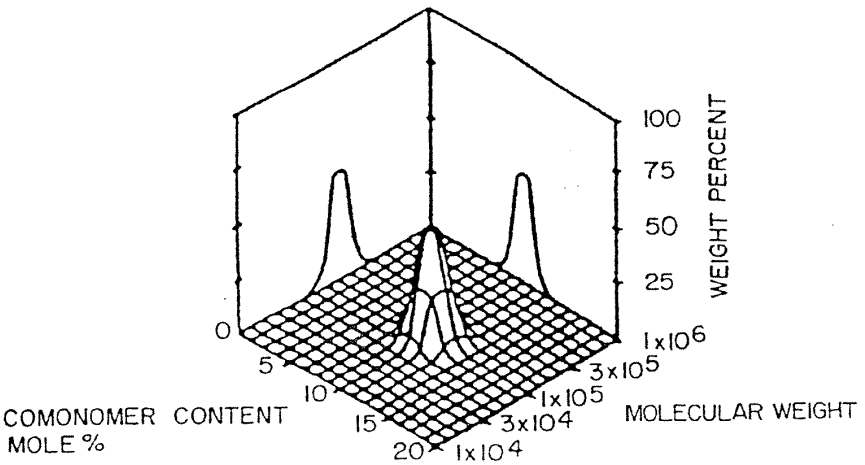


FIG. 2

Case 1:05-cv-00737-JJF Document 159-5 Filed 09/03/2008 Page 34 of 69

EXHIBIT PAGE 000632

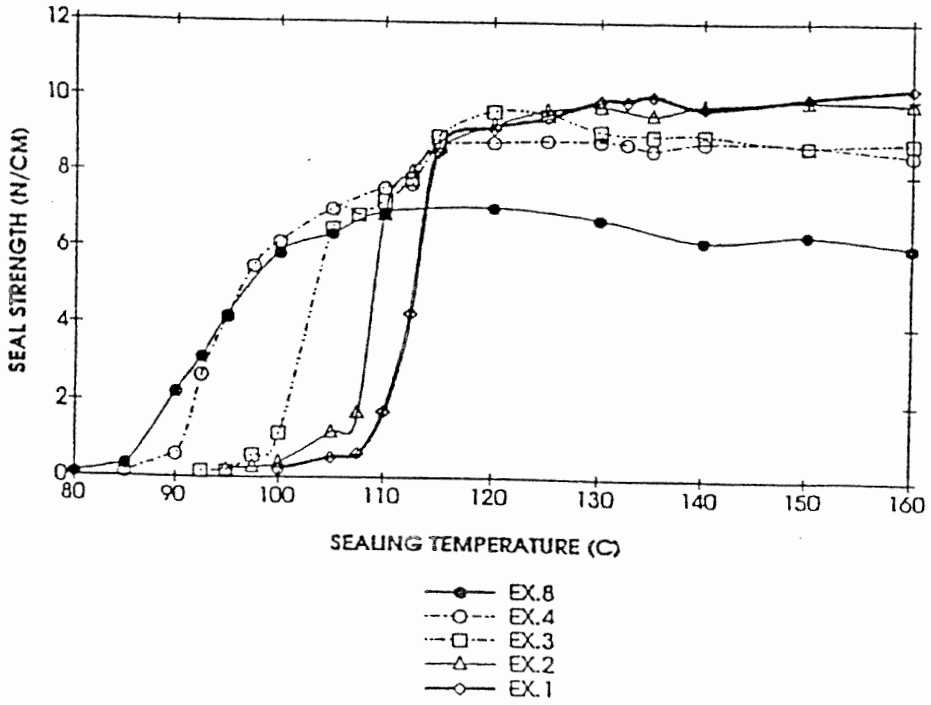

SEAL STRENGTH (N/CM)
12
10
8
6
4
2
0
80
90
100
110
120
130
140
150
160
SEALING TEMPERATURE (C)
EX.8
EX.4
EX.3
EX.2
EX.1

FIG. 3

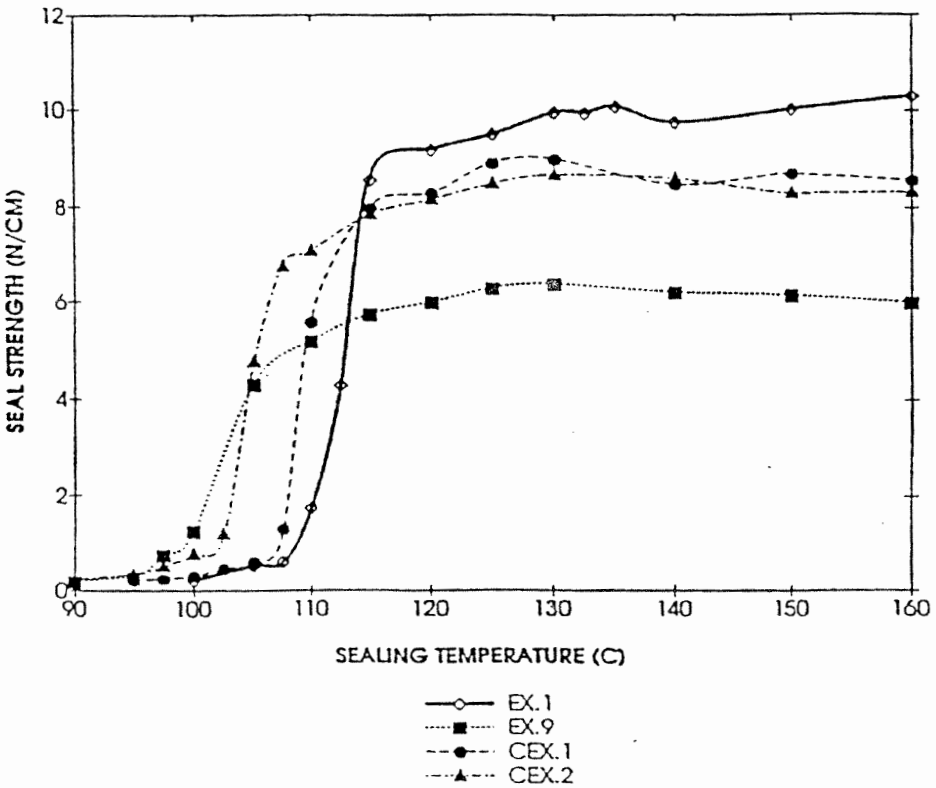

SEAL STRENGTH (N/CM)
12
10
8
6
4
2
0
90
100
110
120
130
140
150
160
SEALING TEMPERATURE (C)
EX.1
EX.9
CEX.1
CEX.2

FIG. 4

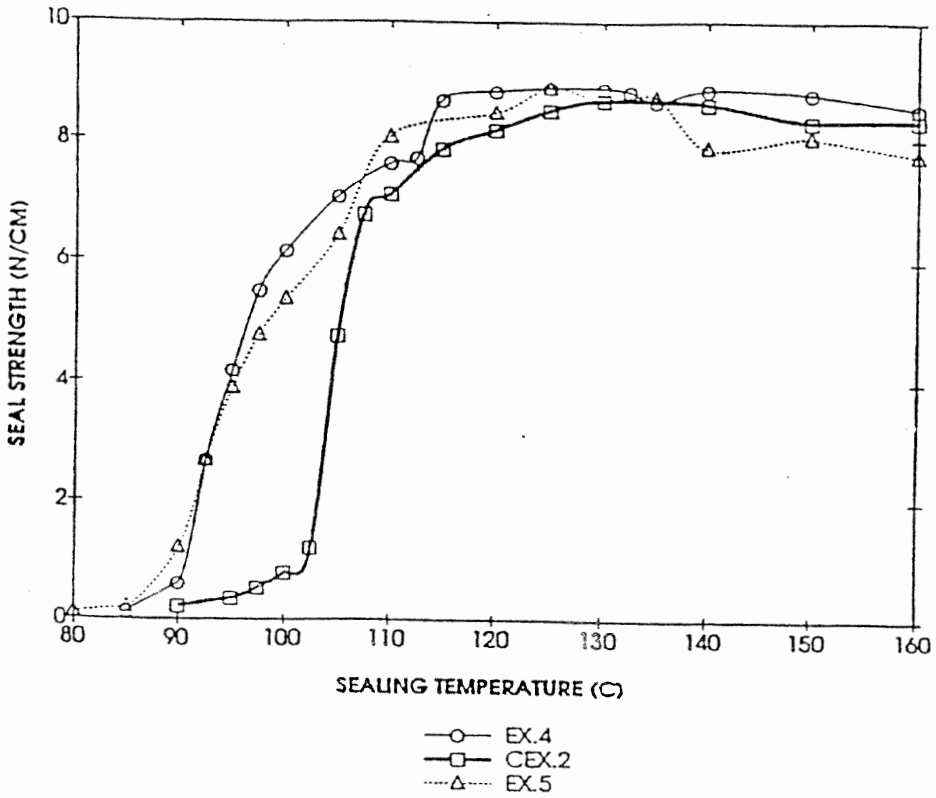


FIG. 5

SUBSTITUTE SHEET (RULE 26)

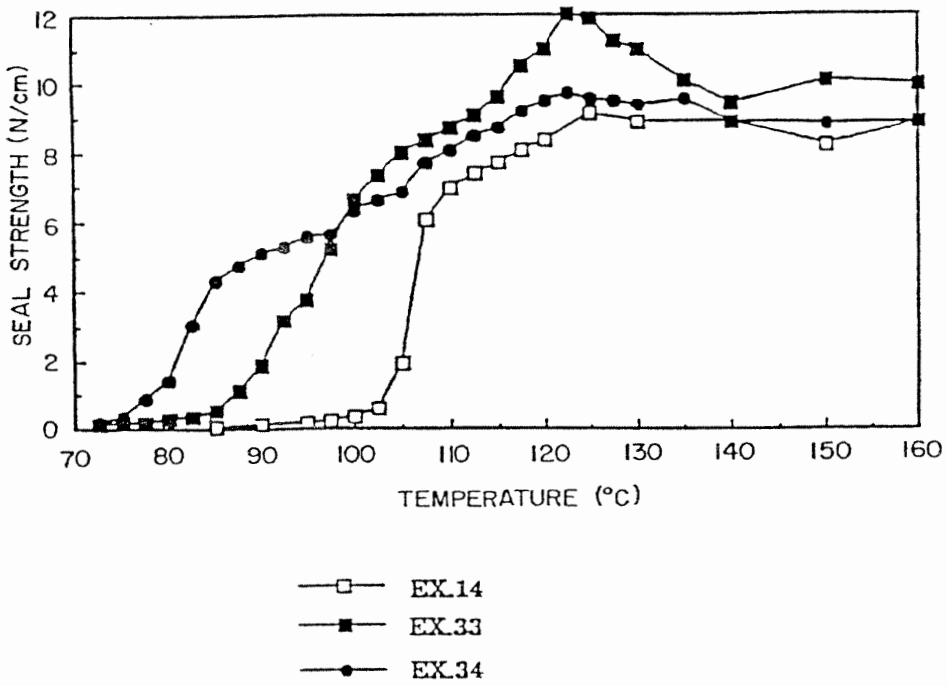

SEAL STRENGTH (N/cm)
0
2
4
6
8
10
12
70
80
90
100
110
120
130
140
150
160
TEMPERATURE (°C)
EX.14
EX.33
EX.34

FIG. 6

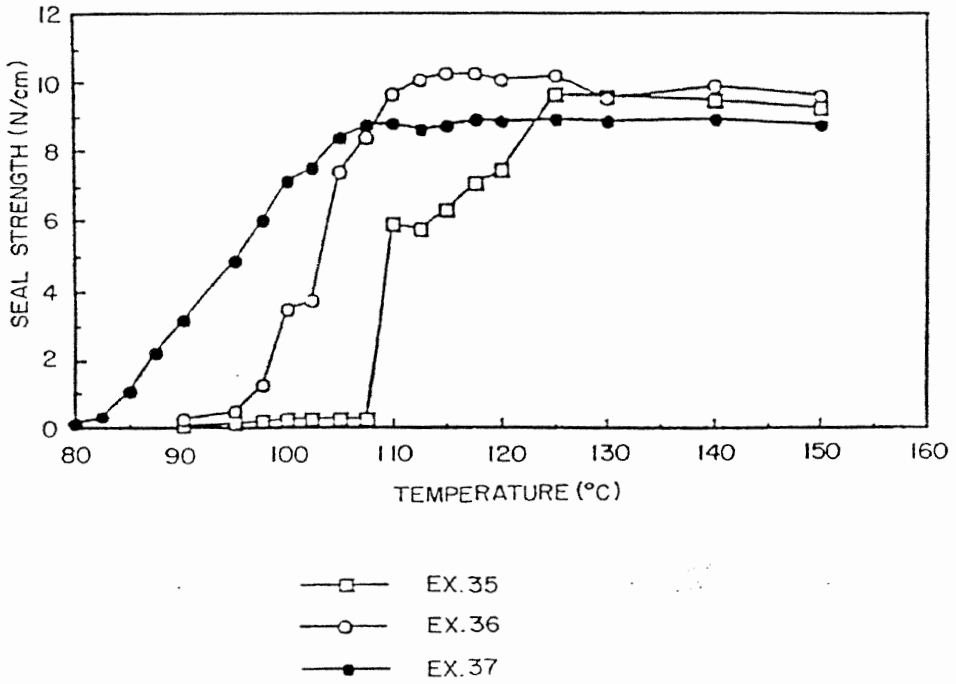

SEAL STRENGTH (N/cm)
0
2
4
6
8
10
12
80
90
100
110
120
130
140
150
160
TEMPERATURE (°C)
EX.35
EX.36
EX.37

FIG. 7

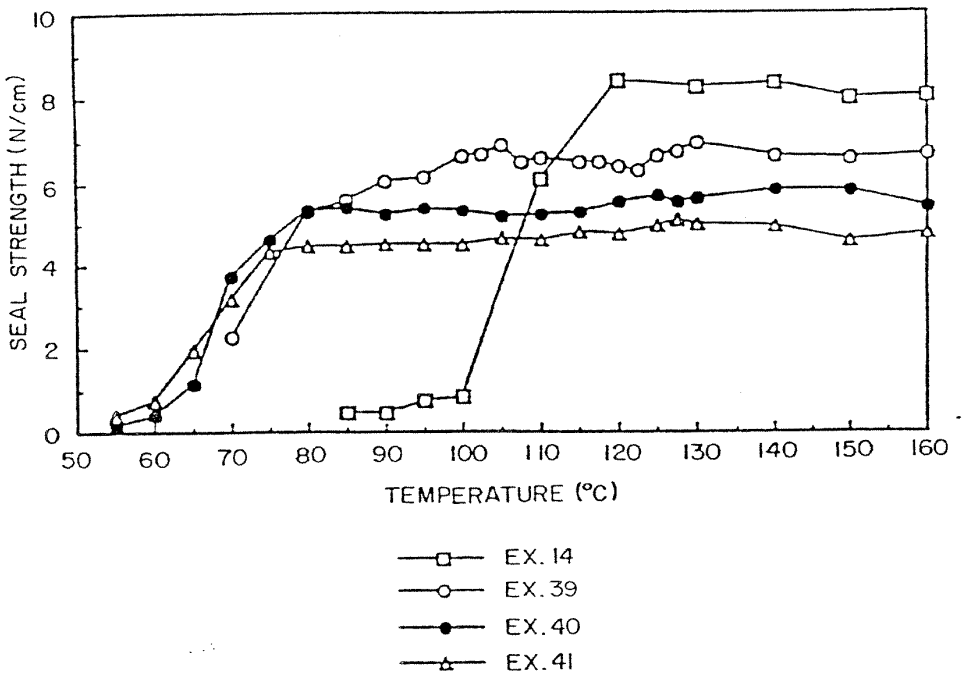

SEAL STRENGTH (N/cm)
0
2
4
6
8
10
50
60
70
80
90
100
110
120
130
140
150
160
TEMPERATURE (°C)
EX. 14
EX. 39
EX. 40
EX. 41

FIG. 8

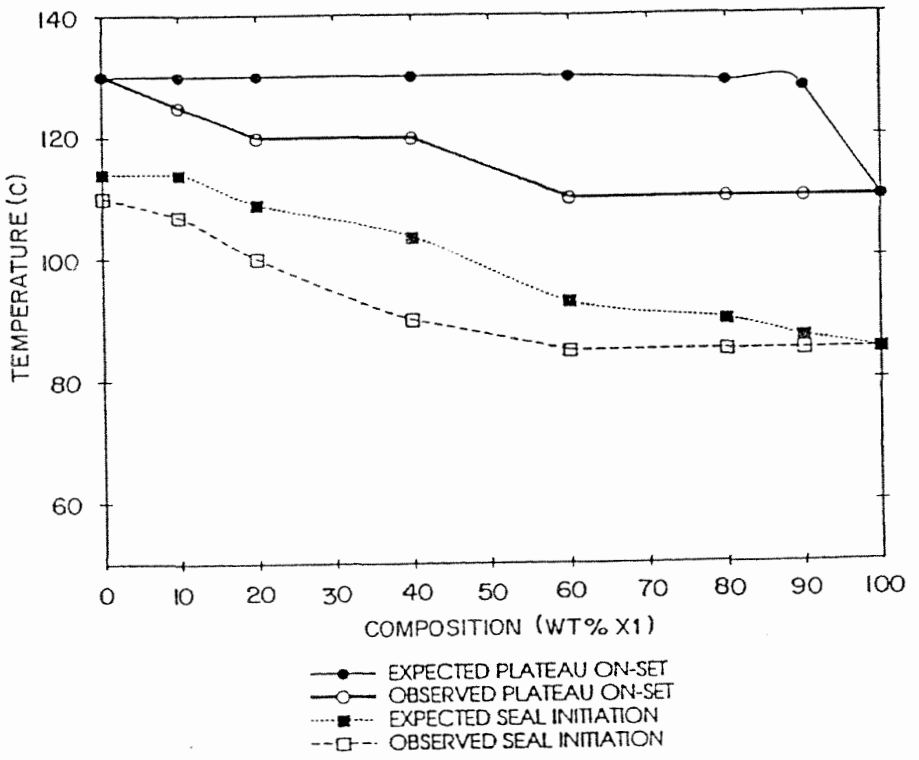

140
120
100
80
60
TEMPERATURE (C)
0
10
20
30
40
50
60
70
80
90
100
COMPOSITION (WT% X1)
EXPECTED PLATEAU ON-SET
OBSERVED PLATEAU ON-SET
EXPECTED SEAL INITIATION
OBSERVED SEAL INITIATION

FIG. 8A

FIG. 9

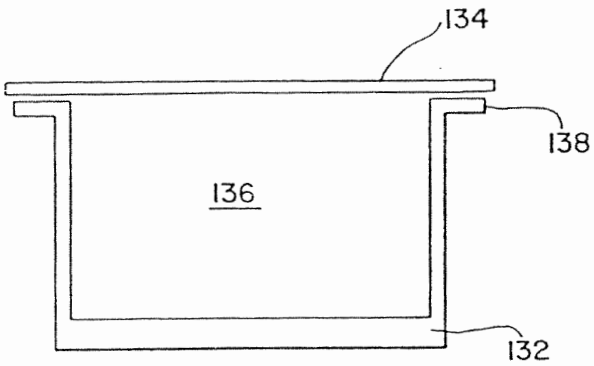
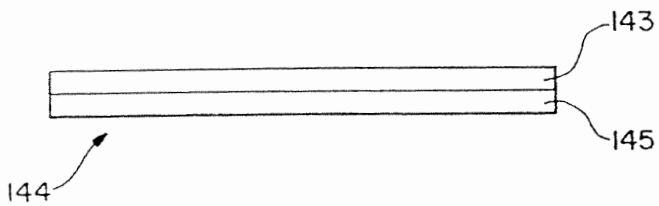


FIG. 10



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 94/10373

A. CLASSIFICATION OF SUBJECT MATTER

C 08 L 23/04,C 08 L 23/08,C 08 L 23/14,C 08 J 5/18

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 L 23/00,C 08 J

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RESEARCH DISCLOSURE, issued November 1983, abstract no. 23 532. --	1,3, 5-7
X,P	WO, A, 94/06 857 (EXXON CHEMICAL PATENTS INC.) 31 March 1994 (31.03.94), claims. --	1-7
A	WO, A, 93/03 093 (EXXON CHEMICAL PATENTS INC.) 18 February 1993 (18.02.93), claims; page 52, lines 32-35 (cited in the application). ----	1-5, 7-10

☐ Further documents are listed in the continuation of box C. ☐ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 November 1994	15. 12. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	WEIGERSTORFER e.h.

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(54) Title: ETHYLENE INTERPOLYMER POLYMERIZATIONS

(57) Abstract

A new process of interpolymerizing ethylene interpolymer products having improved properties, such as increased onset of crystallization temperature, is disclosed. Preferably, the process comprises interpolymerizing a first homogeneous ethylene/alpha-olephin interpolymer and at least one second homogeneous ethylene/alpha-olephin interpolymer using at least two constrained geometry catalysts having different reactivities such that the first ethylene/alpha-olephin interpolymer has a narrow molecular weight distribution (NMWD) with a very high comonomer content and relatively high molecular weight and the second ethylene/alpha-olefin interpolymer has a NMWD with a low comonomer content and a molecular weight lower than that of the first interpolymer. The resultant first homogeneous interpolymer is combined with the resultant second homogeneous interpolymer in appropriate weight ratios resulting in the desired finished polymer structure. The first interpolymer and the second interpolymer can be polymerized in a single reactor or they can be polymerized in separate reactors operated in parallel or series.

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ETHYLENE INTERPOLYMER POLYMERIZATIONS

This invention relates to processes of manufacturing ethylene interpolymer products which have improved properties, especially increased onset of crystallization temperature. The ethylene interpolymer products are made by a polymerization with two or more constrained geometry catalysts having varying reactivities. The interpolymer products can also be made by polymerization reactions in two or more separate, parallel reactors, with the resultant interpolymers intimately combined.

Thermoplastic polymers can be classified as semi-crystalline (at least partly crystalline), highly crystalline, or wholly or mainly amorphous. Crystalline or semi-crystalline polymers typically have a distinct melting point, as measured by differential scanning calorimetry (DSC). Crystalline and semi-crystalline polymers are typically melt-processed into fibers, films or molded articles.

Controlling the nucleation and crystallization rates of the polymers during melt processing is important in determining the physical properties of the finished article. Various methods of controlling nucleation and crystallization have been attempted, usually incorporating nucleating agents (for example, inactive (physical) or active (chemical)) or completely changing polymers. Physical nucleating agents are typically finely divided particles and have a melting and freezing temperature greater than that of the polymer in which the particles are utilized while the chemical nucleating agents are primarily combinations of acidic and basic compounds such as organic or inorganic compounds. Unfortunately, the particulate nucleating agents can also detrimentally affect the physical properties of the final product, for example by lowering the tensile strength of film made from the polymers.

Copending Application Serial Number 07/609,286, filed November 5, 1990, has solved this particulate nucleation problem by blending linear polyethylene with other polyethylenes to cause the blend to have an increased onset of crystallization. While this process is effective, economic considerations can also affect the ability of polymers to be melt blended cost effectively.

Many methods of polymerizing polymers and forming polymer blends to do specific jobs are disclosed in the literature. For example, U.S. Patent 4,937,299 (Ewen et al.) teaches the use of a homogeneous catalyst system comprising at least two different mono-, di- or tricyclopentadienyls and their derivatives of a Group 4b, 5b and 6b transition metal each having different reactivity ratios and aluminoxane. The catalyst system is described as being homogeneous in a solution polymerization system and that the soluble (i.e., homogeneous) catalyst can be converted to a heterogeneous catalyst system by depositing it on a catalyst support. Thus, U.S. Patent 4,937,299 describes their homogeneous catalyst system as a soluble catalyst system.

International Patent Application Number PCT/US89/04259 (Stehling et al.) discloses linear ethylene interpolymer blends of interpolymers having narrow molecular weight distributions and narrow composition distributions. The components of the blends are said to have narrow molecular weight distributions (i.e., the ratio of the weight average molecular weight to the number average molecular weight is less than or equal to 3.0). The components are said to be prepared by using metallocene catalyst systems known to provide narrow composition distributions and narrow molecular weight distributions. The desirable molecular weight and composition distributions are said to be obtained by blending different components or by polymerization of the blend components in the same or multiple reactors.

A new ethylene polymerization process has now been discovered to produce ethylene polymer products having many improved properties, including increased onset of crystallization temperature.

The ethylene polymerization process comprises the steps of:

(a) polymerizing a first homogeneous ethylene polymer using a first activated constrained geometry catalyst composition having a first reactivity such that the first polymer has a melt index of from 0.05 to 50 grams/10 minutes,

(b) polymerizing at least one second homogeneous ethylene polymer using a second activated constrained geometry catalyst composition having a second reactivity such that the second ethylene polymer has a melt index of from 0.05 to 50 grams/10 minutes, and

(c) combining from 50 to 95 weight percent of the first ethylene polymer with from 5 to 50 weight percent of the second ethylene polymer to form an ethylene polymer product.

Preferably, the homogeneous ethylene polymers are ethylene/alpha-olefin interpolymers.

The polymerized ethylene and interpolymerized ethylene/alpha-olefin products have increased onset of crystallization temperature as well as improved cling and low hexane extractables when converted to film form.

The activated constrained geometry catalyst compositions used in the interpolymerization process of the present invention can be made and injected separately into

separate polymerization reactors, or, preferably, injected separately into the same polymerization reactor, or, especially, they can be injected together into the same polymerization reactor.

Figure 1 shows a differential scanning calorimetry melting curve for a homogeneous interpolymer of the present invention.

Figure 2 shows a differential scanning calorimetry melting curve for a comparative heterogeneous polymer.

The homogeneous polymers and interpolymers of the present invention are herein defined as defined in USP 3,645,992, the disclosure of which is incorporated herein by reference. Accordingly, homogeneous interpolymers 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, whereas heterogeneous interpolymers are those in which the interpolymer molecules do not have the same ethylene/comonomer ratio.

In addition, the homogeneous interpolymers of the present invention have a melting curve which resembles that depicted in Figure 2 (i.e., a single melting peak), as opposed to the multiple melting peak demonstrated by a comparative heterogeneous polymer shown in Figure 3.

The homogeneous polymers used to make the novel polymer products of the present invention can be ethylene homopolymers or, preferably, interpolymers of ethylene with at least one C_3-C_{20} α-olefin and/or C_4-C_{18} diolefins. The homogeneous interpolymers of the present invention can also be interpolymers of ethylene with at least one of the above C_3-C_{20} α-olefins and/or diolefins. 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. Therefore, in another aspect, the invention is a process for preparing an ethylene/alpha-olefin terpolymer product, comprising the steps of:

(a) interpolymerizing ethylene, a first comonomer and a second comonomer to form a homogeneous terpolymer using a first activated constrained geometry catalyst composition having a first reactivity and a second activated constrained geometry catalyst composition having a second reactivity to form an ethylene/alpha-olefin terpolymer product, and

(b) recovering the ethylene/alpha-olefin terpolymer product.

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

tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (for example, cyclopentene, cyclohexene and cyclooctene).

The density of the homogeneous polymers used to make the novel interpolymer products of the present invention can be any density appropriate to the selected end use application, for example higher density products for higher modulus applications. Preferably the density is from 0.88 grams/cubic centimeter (g/cm^3) to 0.965 g/cm^3. Density measurements are determined herein according to ASTM D-792.

The molecular weight of the homogeneous polymers used to make the novel polymer products of the present invention is usually indicated and measured by melt index. The melt index is according to ASTM D-1238, Condition (E) (i.e., 190°C/2.16 kilograms) and is also known as I_2. The I_2 of the homogeneous polymers used to make the novel interpolymer products of the present invention can also be convenient to the chosen end use application, but preferably is from 0.01 grams/10 minutes to 1000 g/10 minutes.

The melt flow ratio is indicated and measured by I_{10}/I_2 according to ASTM D-1238, Conditions (N) (190°C/10 kilograms) and (E), respectively. The I_{10}/I_2 of the novel polymer products of the present invention can also be conveniently chosen specific to the desired end use application, but preferably is from 6 to 16. Accordingly, the I_{10}/I_2 ratios of the specific homogeneous polymers used to make up the novel interpolymer products can be appropriately selected.

The first process disclosed herein for producing the novel interpolymer products is also effective when using at least two reactors, especially when a first reactor and a second reactor are operated in series, i.e., one after the other. The first process is also particularly effective when both the ethylene copolymers of (a) and (b) are ethylene/alpha-olefin interpolymers.

A preferred interpolymerization process of the present invention comprises the steps of:

(a) polymerizing a first homogeneous ethylene/alpha-olefin interpolymer using a first constrained geometry catalyst having a first reactivity such that the first interpolymer has from 5 to 30 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point less than 110°C, preferably from 70°C to 110°C,

(b) polymerizing at least one second homogeneous ethylene/alpha-olefin interpolymer using a second constrained geometry catalyst having a second reactivity such that the second ethylene/alpha-olefin interpolymer has from 2 to 10 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point greater than 115°C, preferably from 115°C to 130°C, and

(c) combining from 50 to 95 weight percent of the first ethylene/alpha-olefin interpolymer with from 5 to 50 weight percent of the second ethylene/alpha-olefin interpolymer to form an ethylene/alpha-olefin interpolymer product.

When the interpolymers made in steps (a) and (b) are combined, an ethylene/alpha-olefin interpolymer product is formed having from 5 to 20 weight percent comonomer content, a melt index of from 0.5 to 50 grams/10 minutes, and an I_{10}/I_2 ratio of from 6 to 12 and, preferably, an Mw/Mn of from 2 to 6, and especially from 3 to 6. More preferably, the first homogeneous ethylene/alpha-olefin interpolymer made in step (a) has a narrow molecular weight distribution (NMWD) (i.e., $2 \leq M_w/M_n \leq 5$ with a very high comonomer content (i.e., $10 \leq$ comonomer content ≤ 30) and relatively high molecular weight (i.e., $0.05 \leq I_2 \leq 5$) and the second homogeneous ethylene/alpha-olefin interpolymer made in step (b) has a NMWD (i.e., $2 \leq M_w/M_n \leq 5$) with a low comonomer content (i.e., $2 \leq$ comonomer content ≤ 6) and a molecular weight lower than that of the first interpolymer.

The use of the dual reactivity constrained geometry catalysts can produce interpolymer products that satisfy a variety of requirements such as:

(i) improved nucleation of polymers by adding a medium molecular weight, linear fraction, polyethylene;

(ii) improved cling potential for stretch-cling polymers by producing an interpolymer fraction with a low molecular weight (MW) and high branch content;

(iii) improved ultra low density polyethylene (ULDPE) by making a high MW fraction with a medium branch content which would improve film properties but not increase hexane extractables;

(iv) improved optical properties (for example, clarity and haze), even for thermally formed articles made from the interpolymer products having higher densities; and

(v) higher modulus of thermally formed articles made from the interpolymer product blends.

The interpolymer products made by polymerizing in two separate reactors and subsequently combining melt streams (parallel reactors) yields composite interpolymer product blends. At least one part of the composite interpolymer product blend, preferably from about 20-80 percent of the blend, has a melting point less than about 115°C, while at least another part of the blend has a melting point greater than about 120°C.

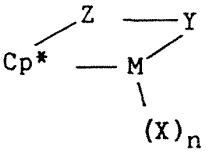
Constrained geometry catalyst preparation is described in detail in United States Application Serial Numbers 401,345 and 401,344, both filed August 31, 1989; SN 428,082, SN 428,283 and SN 428,276, all filed October 27, 1989; SN 436,524, filed November 14, 1989; SN 545,403, filed July 3, 1990; and SN 776,130, filed October 15, 1991. The disclosures of all of these U.S. Applications are incorporated herein by reference.

Suitable catalysts for use herein preferably include constrained geometry catalysts as disclosed in U.S. Application Serial Nos.: 545,403, filed July 3, 1990; 758,654, filed September 12, 1991; 758,660, filed September 12, 1991; and 720,041, filed June 24, 1991, the teachings of all of which are incorporated herein by reference. The monocyclopentadienyl transition metal

olefin polymerization catalysts taught in USP 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 generally 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, preferably a metal of groups 3-6, and especially a metal of groups 4 and 5, 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;

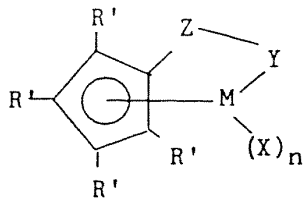
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

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 M comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system.

More preferably still, such complexes correspond to the formula:



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

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

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

M is 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:

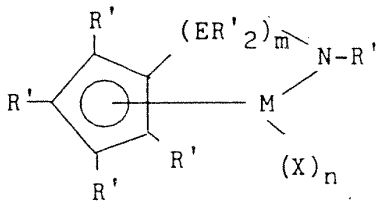
R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and

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)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido)(tetramethyl-η^5-cyclopentadienyl)methylene-titanium 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.

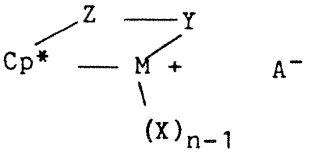
In a preferred embodiment, the metal compound is MX_{n+1}, that is M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. 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 July 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 October 15, 1991 and the copending application entitled: "Preparation of Metal Coordination Complex (II)", filed in the names of Peter Nickias and David Devore, on October 15, 1991, the teachings of which are incorporated herein by reference thereto.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Preferred catalyst compositions are formed using cocatalysts which 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 and phosphorus which exhibit semi-metallic characteristics.

Illustrative, but not limiting examples of monocyclopentadienyl metal components (first components) which may be used in the preparation of cationic complexes are derivatives of titanium, zirconium, vanadium, hafnium, chromium, lanthanum, etc. Preferred components are titanium or zirconium compounds. Examples of suitable mono-cyclopentadienyl metal compounds are hydrocarbyl-substituted monocyclopentadienyl metal compounds such as (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyl-zirconium 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)methylene-titanium 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-amide, or cyclopentadienyl-silane amide compound. The reaction is conducted in an inert liquid such as tetrahydrofuran, C_{5-10} alkanes, toluene, etc. utilizing conventional synthetic procedures. Additionally, the first components may be prepared by reaction of a group II derivative of the cyclopentadienyl compound in a solvent and separating the salt by-product. Magnesium derivatives of the cyclopentadienyl compounds are preferred. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. The resulting metal cyclopentadienyl halide complexes may be alkylated using a variety of techniques. Generally, the metal cyclopentadienyl alkyl or aryl complexes may be prepared by alkylation of the metal cyclopentadienyl halide complexes with alkyl or aryl derivatives of group I or group II metals.

Preferred alkylating agents are alkyl lithium and Grignard derivatives using conventional synthetic techniques. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. A preferred solvent is a mixture of toluene and tetrahydrofuran.

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

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

$$(L\text{-}H)^{+}\ [A]^{-}$$

wherein:

L is a neutral Lewis base;

$(L\text{-}H)^{+}$ 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:

$$[L\text{-}H]^+ [BQ_4]^-$$

wherein:

L is a neutral Lewis base;

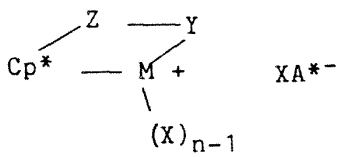
$[L\text{-}H]^+$ is a Bronsted acid;

B is boron in a valence state of 3; and

Q is as previously defined.

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

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



wherein:

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

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

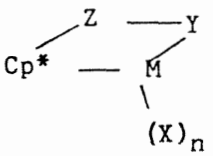
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

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

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

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

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



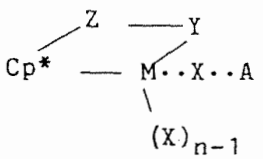
wherein:

Cp*, M, and n are as previously defined,

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

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

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



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

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

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

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

Preferably, monocyclopentadienyl metal coordination complexes of groups 3, 4, 5 or lanthanide metals according to the present invention have constrained geometry such that the angle, Θ, between the centroid of the Cp* group and the Y substituent is less than 115°, more preferably less than 110°, most preferably less than 105°, and especially less than 100°.

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

It is important that the specific constrained geometry catalysts chosen for polymerizing the ethylene polymers or ethylene/alpha-olefin interpolymers be of differing reactivities. The differing reactivities can be achieved by using the same constrained geometry catalyst composition, and polymerizing at different reactor temperatures, or, preferably, by using two distinctly different catalysts which have different reactivity. For example, when the active metal site is selected from the group consisting of Ti, V, Hf and Zr, the reactivity of the active metal site will be in that order: Ti is more reactive than V, which in turn is more reactive than Hf, which in turn is more reactive than Zr. Accordingly, the polymer density will also increase in that same order, with a polymer made using a constrained geometry catalyst containing Zr having a higher density than a polymer made using a constrained geometry catalyst containing Ti. Obviously, other combinations of metal atoms are possible, such as combining Ti with Hf, or combining V with Zr. The instant invention is not limited to any particular combination of constrained geometry catalysts, with the stipulation that the selected constrained geometry catalysts have differing reactivities.

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.

Additives, such as anti-oxidants, slip agents, anti-block agents, pigments (for example, titanium dioxide), wetting agents (as disclosed, for example, in USP 4,578,414, and in USP 4,835,194, the disclosures of which are incorporated herein by reference) may be incorporated into the homogeneous polymers used to make the novel interpolymer products of the present invention to the extent that they do not interfere with the crystallization kinetic improvements demonstrated herein.

Fabricated (for example, thermally formed) articles can be advantageously made from these novel interpolymer products. These articles include films (for example, blown films,

cast films, or extrusion coated films), molded articles (for example, injection molded, blow molded, or roto molded articles), and fibers (for example, melt blown, spunbond, or staple fibers and fabrics made from these fibers). Skilled artisans in the processability of conventional thermoplastics can readily form a variety of fabricated articles from these interpolymer products. In particular, the increased onset of crystallization temperature of these novel interpolymer products has utility in making fabricated articles which are rapidly cooled, for example, blown film (control of the freeze line) or melt spun fibers (where the high surface area of the fibers and the limited quench air capabilities are often in conflict).

The whole interpolymer product samples and the individual interpolymers samples are 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.

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

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

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

$$M_w = R w_i * M_i$$

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

The crystallization onset temperatures of the blend components (i.e., the homogeneous polymers and interpolymers) and of the polymer and interpolymer products of the present invention are measured using differential scanning calorimetry (DSC). Each sample to be tested is made into a compression molded test plaque according to ASTM D 1928. The plaques are then microtomed at room temperature using a Reichert Microtome or razor blade to obtain samples having a thickness of about 15 microns. About 5 milligrams of each sample to be tested is placed in the DSC pan and heated to about 180°C, held at that temperature for 3 minutes to destroy prior heat history, cooled to -50°C at a rate of 10°C/minute and held at that temperature for 2 minutes. The crystallization onset temperature and the peak temperature are recorded by the DSC as the temperature at which crystallization begins and the temperature at which the sample is as fully crystallized as possible, respectively, during the

cooling period from 180°C to -50°C. The sample is then heated again from -50°C to 140°C at a rate of 10°C/minute to record the heat of fusion and calculate total percent crystallinity. For polyethylene, the percentage crystallinity is obtained using the latent heat of fusion equal to 292 Joules/gram for 100 percent crystalline linear polyethylene.

Preparation of (t-Butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dichloride

Step 1

(Chloro)(dimethyl)(tetramethylcyclopentadi-2,4-enyl)silane

To a solution of 21.5 g (167 mmol) dimethyldichlorosilane in 150 mL THF cooled to -40°C was slowly added a solution of 8.00 g (55.6 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 80 mL THF. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil.

Step 2

(t-Butylamino)(dimethyl)(tetramethylcyclopentadi-2,4-enyl)silane

A solution of 11.07 g (151 mmol) t-butyl amine in 20 mL THF was added during 5 minutes to a solution of 13.00 g (60.5 mmol) (chloro)(dimethyl)(tetramethylcyclo-pentadienyl)silane in 300 mL THF. A precipitate formed immediately. The slurry was stirred for 3 days, then the solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil.

Step 3

Dilithium (tert-butylamido)(dimethyl)(tetramethylcyclo-pentadienyl)silane

To a solution of 3.000 g (11.98 mmol) (t-Butylamino)(dimethyl)(tetramethylcyclopentadienyl)-silane in 100 mL ether was slowly added 9.21 mL of 2.6 M (23.95 mmol) butyl lithium in mixed C_6 alkane solvent. A white precipitate formed and the reaction mixture was stirred overnight, then filtered. The solid was washed several times with ether then dried under reduced pressure to give the product as a white powder.

Step 4

(t-Butylamido)dimethyl(tetramethyl-η^5-

-cyclopentadienyl)silane titanium dichloride

0.721 g (3.80 mmol) Of $TiCl_4$ was added to 30 mL frozen (-196°C) THF. The mixture was allowed to warm to -78°C (dry ice bath). To the resulting yellow solution was slowly added a solution of 1.000 g (3.80 mmol) dilithium (t-butylamido)(dimethyl)tetra-methylcyclopentadienyl)silane in 30 mL THF. The solution was allowed to warm to room temperature while stirring overnight. The solvent was removed from the resulting very dark solution. The residue was extracted with pentane and filtered. Cooling in a freezer caused the

separation of a very soluble dark reddish-brown material from a light yellow-green crystalline solid. The solid was filtered out and recrystallized from pentane to give the olive-green catalyst complex product.

Methylaluminoxane (obtained commercially from Schering AG and designated herein as MAO) 10 percent by weight in toluene, is used in the examples described herein as a cocatalyst together with the catalyst complex to form the activated Ti stock solution catalyst mixture. (Other MAO preparations are disclosed, for example, in USP 5,041,583, USP 5,041,584 and USP 5,041,585, the disclosures of which are incorporated herein by reference.) The catalyst composition mixture is mixed for a few minutes and transferred by syringe to a catalyst injection cylinder on the polymerization reactor.

The compositions described in Table 2 are prepared with the same Ti stock solution and varying amounts of MAO solution and isoparaffinic solvent. Table 3 shows examples of a zirconium catalyst prepared in a similar manner from an equivalent complex ([Zr] = 0.005 M) and the same MAO stock solution.

A stirred, one-gallon (3.79L) autoclave reactor is charged with two liters of an isoparaffinic hydrocarbon (Isopar™ E made by Exxon) and the alpha-olefin comonomer before heating to the temperature specified in Table 1. Hydrogen (10 mmol) is then added to the reactor, followed by ethylene sufficient to bring the total pressure to 450 pounds per square inch gauge (psig) (3204 kPa). An amount of the selected mixed constrained geometry activated catalyst mixture, as described under the catalyst complex preparation section herein, is injected into the reactor. The reactor temperature and pressure are maintained constant at the desired final pressure and temperature by continually feeding ethylene during the polymerization run and cooling the reactor as necessary. After a 10 minute reaction time, the ethylene is shut off and the hot solution transferred into a nitrogen-purged resin kettle. After drying, the samples are then weighed to determine catalyst efficiencies followed by melt index (ASTM D-1238, condition 190°C/2.16 kg) and density (ASTM D-792) measurements. The polymerization reaction conditions specified in Table 1 are used for both sets of homogeneous copolymers listed in Tables 2 and 3.

Table 1
Polymerization conditions for single catalyst runs

Ex.	Reactor Temp. (°C)	Octene (moles)	Hydrogen (mmol)	Al:M* Ratio
1 & 1A	150	2.5	10	500
2 & 2A	150	2.5	10	500
3 & 3A	130	1	10	500
4 & 4A	130	1	10	250
5 & 5A	130	1	10	100

*M = selected metal atom (e.g., Ti or Zr)

Properties of some of the homogeneous copolymers made by using only a titanium based constrained geometry catalyst are listed in Table 2, while properties of the homogeneous copolymers made by using only a zirconium based constrained geometry catalyst are listed in Table 3. Even though the comonomer 1-octene is added to each separate reaction, very little of the 1-octene is incorporated into the copolymer when the catalyst is a zirconium catalyst (indicated by higher interpolymer density), due to the lower reactivity of the zirconium catalyst. The copolymers made using the titanium based constrained geometry catalyst have lower densities, indicating higher incorporation of 1-octene and higher reactivity of the titanium catalyst.

Table 2
Copolymer properties
using titanium constrained geometry catalyst

Ex.	Titanium (mmol)	Density (g/cm^3)	I_2 (g/10 min)	Melt Point (°C)	M_w	M_n	M_w/M_n
1	0.02	0.9130	13.6	94.7	51000	14000	3.64
2	0.02	0.9121	10.1	95.9	53700	14700	3.65
3	0.02	0.9198	0.18	108.8	105000	23200	4.53
4	0.02	0.9197	0.15	109.8	136000	29400	4.63
5	0.02	0.9153	0.15	104.9	146000	26300	5.55

Table 3
Copolymer properties
using zirconium constrained geometry catalyst

Ex.	Zirconium (mmol)	Density (g/cm^3)	Melt Index (g/10 min)	Melt Point (°C)	M_w	M_n	M_w/M_n
1A	0.020	0.9468	98.9	123.9	39800	7470	5.33
2A	NM	NM	NM	NM	NM	NM	NM
3A	0.005	0.9556	20.6	128.7	62200	14000	4.44
4A	0.010	0.9533	12.2	128.4	60100	16800	3.58
5A	0.020	0.9519	11.5	128.6	56900	17100	3.33

NM = Not Measured

The constrained geometry catalysts can be used to polymerize the interpolymer products of the present invention in multiple reactor configurations as well. For example, one constrained geometry catalyst can be injected into one reactor and another constrained geometry catalyst having a different reactivity injected into another reactor. Or, the same constrained geometry catayst can be injected into more than one reactor and the reactors operated at differing temperatures to effect differing catalyst reactivities.

Such multiple reactor schemes are well known to those skilled in the art of ethylene interpolymerization. For example, series and parallel dual reactor polymerizations are disclosed in USP 3,914,342, the disclosure of which is incorporated herein by reference.

A stirred, one-gallon (3.79L) autoclave reactor is charged with two liters of an isoparrafinic hydrocarbon (for example, Isopar® E made by Exxon) and the selected alpha-olefin comonomer before heating to the temperature specified in Table 4. Hydrogen (10 mmol) is then added to the reactor, followed by ethylene sufficient to bring the total pressure to 450 pounds per square inch gauge (psig) (3204 kPa). An amount of the mixed constrained geometry activated catalyst mixture (as described under catalyst activation) is injected into the reactor. The reactor temperature and pressure are maintained constant at the desired final pressure and temperature by continually feeding ethylene during the polymerization run and cooling the reactor as necessary. After a 10 minute reaction time, the ethylene is shut off and the hot solution transferred into a nitrogen-purged resin kettle. After drying, the samples are then weighed to determine catalyst efficiencies followed by melt index and density measurements.

Examples 6-12 are examples of ethylene/1-octene polymerizations performed in a single reactor, using a single injection of an activated mixture of constrained geometry catalysts (titanium and zirconium) at a methylaluminoxane (MAO):total catalyst metal ratio of

500:1 and are described in Table 4. Surprisingly, compression molded films made from the novel interpolymer product of Example 10 had a specular transmission (i.e., clarity) (ASTM D 1746) of about 4, while for compression molded films made from the novel interpolymer product of Examples 11 and 12, the specular transmission was less than about 1. The higher reactor polymerization temperature used to make the interpolymer product of Example 10 (160°C) therefore improves the specular transmission of film made therefrom, especially when compared withe film made from interpolymer products polymerized at temperatures lower than about 160°C.

Example 13 is a comparative example using only a single constrained geometry catalyst (MAO:Ti ratio of 500:1) at a single reaction temperature (110°C).

Example 14 illustrates the use of a single activated constrained geometry (Titanium at MAO:Ti ratio of 500:1) catalyst at two different reactor temperatures (110°C and 150°C).

Examples 15-19 show ethylene/1-octene interpolymerizations using mixed constrained geometry catalysts (Ti and Zr) at MAO:total metal concentrations of 350:1.

Examples 20-22 show data relating to interpolymerizations of ethylene with tetradecene, octadecene and cyclooctene, respectively. For Examples 20 and 21, the MAO:total metal concentration is 500:1 while for Example 22 the MAO: total metal concentraion is 750:1.

Examples 23-25 describe ethylene/1-propene/1-octene terpolymer interpolymerizations, each using a single injection of a mixture of two constrained geometry catalysts (titanium and zirconium), each using methylaluminoxane as a cocatalyst to form the activated catalyst mixture.

Table 4
Polymerizations using 2 constrained geometry catalysts having differing reactivities

Ex.	1-octene (ml)	H_2 (mmol)	mmole Ti	mmole Zr	Ti:Zr ratio	Reactor Temp. (°C)	Sample Weight (grams)	Gradient Density (g/cm^3)	I_2 (g/10 min)	I_{10}/I_2	Cryst. Onset (°C)	M_w/M_n
6	150	10	.016	.004	4:1	130	180	.9280	.7	13.4	112.8	4.81
7	150	10	.0121	.008	3:2	130	180	.9392	1.5	12.3	114.8	4.57
8	300	10	.0046	.016	3.5:1	130	190	.9434	13.2	7.5	114.8	3.22
9	300	10	.008	.002	4:1	130	172	.9261	2.5	10.3	113.5	4.13
10	150	10	.0093	.00125	8:1	160	40	.9367	NM*	NM*	113.3	3.64
11	150	20	.0093	.00125	8:1	130	128	.9260	3.8	9.7	112.7	3.64
12	150	30	.0093	.00125	8:1	100	218	.9250	10.3	7.2	114.5	2.66
13[c]	150	20	.02	0	0	110	209	.9136	.2	15.6	96.3	3.89
14***	150	40	.012	0	0	110/150	172	.9236	13.1	7.2	108.1	2.43
15**	150	30	.019	.001	20:1	130	188	.9195	NM	NM	99.8	NM
16**	150	30	.019	.001	20:1	162	82	NM	NM	NM	104.1	NM
17**	150	10	.019	.001	20:1	160	70	.9290	NM	NM	105.2	NM
18**	150	30	.0095	.0005	20:1	100	105	NM	NM	NM	95.9	NM
19**	150	20	.019	.001	20:1	100	225	.9120	NM	NM	94	NM

MAO: total metal ratio for Examples 6-14 = 500:1
*NM = Not Measured
**MAO:total metal ratio for Examples 15-19 = 350:1
***Half of the catalyst is injected at reactor temp. of 110°C,
then the reactor temp was increased to 150°C and the other half of the catalyst injected
[c] = Comparative Example only

Table 5
Polymerizations using comonomers other than 1-octene
using 2 constrained geometry catalysts having differing reactivities

Ex.	Comonomer (ml added)	mmole Ti	mmole Zr	Ti:Zr ratio	Reactor Temp. (°C)	Sample Weight (grams)	Gradient Density (g/cm^3)	I_2 (g/ 10 min)	MAO: soluble Ti	Cryst. Onset (°C)	M_w/M_n
20	tetradecene (300)	.019	.001	19:1	130	275	.9245	96.8	500:1	96.8	2.86
21	octadecene (300)	.019	.001	19:1	130	250	.9166	45.1	500:1	104.9	3.91
22	cyclooctene (350)	.019	.001	19:1	130	150	.9265	32.3	750:1	121.3	3.65

Table 6
Polymerizations of ethylene/1-propene/1-octene terpolymers
using 2 constrained geometry catalysts having differing reactivities

Ex.	1-octene (ml)	1-propene (gm)	mmole Ti	mmole Zr	Ti:Zr ratio	Reactor Temp. (°C)	Sample Weight (grams)	Gradient Density (g/cm^3)	I_2 (g/10 min)	Cryst. Onset (°C)	M_w/M_n
23	150	40	.019	.001	19:1	130	75	.9051	NF*	103.7	4.62
24	150	20	.019	.001	19:1	140	75	.9158	7	109.2	4.52
25	150	10	.019	.001	19:1	150	75	.9273	21.8	108	4.05

*NF = No Flow (i.e., the molecular weight is very high)
MAO : total metal = 500:1 for Ex. 23-25