



(86) Date de dépôt PCT/PCT Filing Date: 2004/04/14
(87) Date publication PCT/PCT Publication Date: 2005/07/28
(85) Entrée phase nationale/National Entry: 2006/05/18
(86) N° demande PCT/PCT Application No.: US 2004/011455
(87) N° publication PCT/PCT Publication No.: 2005/068076
(30) Priorité/Priority: 2003/12/22 (US10/745,461)

(51) Cl.Int./Int.Cl. *B01J 31/38* (2006.01),
C08F 4/44 (2006.01), *C08F 10/02* (2006.01)
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(54) Titre : COMPOSITIONS DE POLYETHYLENE PRESENTANT DES PROPRIETES DE DECHIREMENT
AMELIOREES

(54) Title: POLYETHYLENE COMPOSITIONS HAVING IMPROVED TEAR PROPERTIES

(57) **Abrégé/Abstract:**

Disclosed is a high density multimodal polyethylene composition that has a density of 0.935 g/cc or more, and that includes a blend of a first polyethylene component and a second polyethylene component, in which: the first polyethylene component includes a bimodal polyethylene; and the second polyethylene component includes a metallocene produced unimodal polyethylene, the composition characterized in having a low level of polyethylene having a molecular weight of less than 1,000 amu and a low level of polyethylene having a molecular weight greater than 500,000 amu.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
28 July 2005 (28.07.2005)

PCT

(10) International Publication Number
WO 2005/068076 A1

(51) International Patent Classification⁷: **B01J 31/38**,
C08F 4/44, 10/02

GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

(21) International Application Number:
PCT/US2004/011455

(22) International Filing Date: 14 April 2004 (14.04.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/745,461 22 December 2003 (22.12.2003) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,

Declarations under Rule 4.17:

— as to the identity of the inventor (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYETHYLENE COMPOSITIONS HAVING IMPROVED TEAR PROPERTIES

(57) Abstract: Disclosed is a high density multimodal polyethylene composition that has a density of 0.935 g/cc or more, and that includes a blend of a first polyethylene component and a second polyethylene component, in which: the first polyethylene component includes a bimodal polyethylene; and the second polyethylene component includes a metallocene produced unimodal polyethylene, the composition characterized in having a low level of polyethylene having a molecular weight of less than 1,000 amu and a low level of polyethylene having a molecular weight greater than 500,000 amu.

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POLYETHYLENE COMPOSITIONS HAVING IMPROVED TEAR PROPERTIES

BACKGROUND

Field of Inventions

5 [0001] Embodiments of the present inventions generally relate to compositions containing polyethylene, and more particularly, to blends of mLLDPE and bimodal polyethylenes.

Description of Related Art

10 [0002] Although bimodal polyethylene compositions have numerous advantages, and have solved various problems in the art, an ongoing need exists for further improvements, particularly in films and polyethylene compositions used to make films. Some of the properties used to characterize films are Elmendorf Tear (MD and TD) values, which are properties based on the procedures set forth in ASTM D 1922. The MD Elmendorf Tear value refers to tear resistance properties in the "machine direction" while the TD Elmendorf Tear value refers to tear resistance properties in the "transverse direction." It is generally desirable to balance the two values. A film that has a highly unbalanced TD/MD ratio, e.g., over 10, is often found to be splitty, and to experience zippering when subjected to tear. At least some of the compositions described herein have improved "tear balance," a term that refers to the TD/MD ratio of a film made from that particular composition. As discussed herein, a composition with a better tear balance is one that can be formed into a film with a lower TD/MD ratio (closer to unity or 1) than a composition with a less advantageous tear balance, such that a film made of 20 the latter composition has a higher, and less desirable, TD/MD ratio.

[0003] Certain patents that refer to polyethylene compositions, and methods for making polyethylene, include the following: U.S. Patent Nos. 4,336,352; 5,091,228; 5,110,685; 5,208,309; 5,274,056; 5,635,262; 5,338,589; 5,344,884; 5,378,764; 5,494,965; 5,739,225; 5,795,941; 6,090,893; 6,340,730; 6,359,072; 6,388,017; 6,388,115; 6,403,717; 6,420,580; 25 6,441,096; 6,476,166; 6,534,604; 6,562,905; 6,605,675; 6,608,149; and WO 97/47682 and WO 94/22948.

SUMMARY

[0004] Various specific embodiments are described herein, and in the claims. Preferred polyethylene compositions herein are blend compositions that include at least one polyethylene that is preferably a bimodal high density polyethylene and at least one polyethylene that is 30

preferably a unimodal polyethylene, as described elsewhere in greater detail. Persons skilled in the polyethylene art know that the type or form of catalyst used influences the molecular structure and properties of the polyethylene, and even slight changes in the type or form of the catalyst can sometimes dramatically affect certain properties of the resulting polyethylene.

5 [0005] Accordingly, one or more specific embodiments of the compositions described herein include a unimodal polyethylene that is made using a metallocene catalyst, or a linear low density polyethylene having the desired characteristics described herein.

[0006] Also, one or more specific embodiments of the compositions described herein include a bimodal polyethylene, which is preferably made using a dual or mixed catalyst
10 system, e.g., one of the dual or mixed catalyst systems described below in greater detail in connection with bimodal polyethylenes. For example, a dual catalyst system useful for forming a bimodal polyethylene is bis(2-(trimethylphenylamido)ethyl)amine zirconium dibenzyl (for a high molecular weight component) and bis(n-propyl Cp) zirconium dichloride (for a low molecular weight component). Bimodal polyethylenes and dual or mixed catalyst
15 systems are also discussed below in greater detail. Further, certain specific embodiments of polyethylene compositions described herein surprisingly have more balanced TD/MD Tear properties than previously prepared polyethylene compositions. Such specific embodiments and the specific TD/MD levels are discussed in greater detail below.

[0007] In the past, compositions prepared by others have included certain types of bimodal
20 polyethylene blended with certain types of unimodal polyethylene. However, films prepared from those compositions have exhibited TD/MD tear ratios that are actually higher (and thus worse) than TD/MD tear ratios of films made from compositions consisting only of bimodal polyethylene. In certain cases, the MD Elmendorf Tear decreases while the TD Elmendorf Tear increases. In contrast, films made from certain embodiments of the compositions
25 described herein include particular types of bimodal polyethylene blended with particular types of unimodal polyethylene. It has been surprisingly discovered that these films have a lower TD/MD tear ratio than the TD/MD tear ratio of films made from a composition that consists only of that particular bimodal polyethylene, or even the TD/MD tear ratio of films made from blends of another type of bimodal polyethylene in combination with a unimodal polyethylene.
30 Such lowering of the TD/MD ratio to a more balanced level is desirable, and without being bound by theory is considered to be attributable at least in part to the particular type of bimodal polyethylene (including those described herein) that is incorporated into the composition.

Also, in certain embodiments the lowering of the TD/MD ratio is due in part to the nature of the unimodal polyethylene that is blended with the bimodal polyethylene. At least one of the factors associated with the improved TD/MD ratio is the particular catalyst system used.

5 [0008] Certain embodiments of the compositions described herein have a balanced TD/MD ratio. Different embodiments of films (including 0.5 mil and 1.0 mil films, as well as other gauges also) made of compositions that include a bimodal polyethylene blended with a unimodal polyethylene have a TD/MD tear ratio of 10 or less; or 9 or less; or 8 or less; or 7 or less; or 6 or less; or 5 or less; or 4 or less; or 3 or less; or 2 or less.

10 [0009] Further, certain embodiments of the composition have a TD Elmendorf Tear, including 0.5 mil and 1.0 mil, falling within one of a number of ranges, including TD Elmendorf Tear having a lower limit of 20, or 40, or 60, or 100, or 200; and an upper limit of 100, or 200, or 300, or 400, or 500, or even in certain embodiments 600, or 700; of 800, or 900, or 1000, or more. Thus, an illustrative range of TD Elmendorf Tear is 50 to 500.

15 [0010] Further, certain embodiments of the composition have an MD Elmendorf Tear, including 0.5 mil and 1.0 mil, that is preferably lower than TD Elmendorf Tear, and that preferably falls within any one of a number of ranges, including MD Elmendorf Tear having a lower limit of 5, or 10, or 15, or 20, or 25, or 30, or 40, or 50; with a an upper limit of 3, or 5, or 8, or 10, or 15, or 20, or 25, or 30, or 35, or 40, or 45, or 50.

DETAILED DESCRIPTION

20 [0011] Density is a physical property of a composition, is determined in accordance with ASTM-D-1505, and is expressed as grams per cubic centimeter (or grams per milliliter).

25 [0012] The term "polyethylene" means a polymer made of at least 50% ethylene-derived units, preferably at least 70% ethylene-derived units, more preferably at least 80% ethylene-derived units, or 90% ethylene-derived units, or 95% ethylene-derived units, or even 100% ethylene-derived units. The polyethylene can thus be a homopolymer or a copolymer, including a terpolymer, having other monomeric units. A polyethylene described herein may, for example, include units derived from a co-monomer that is preferably an α -olefin, e.g., propylene, 1-butene, 1-pentene, 1-hexene, or 1-octene. Other embodiments may include ethacrylate or methacrylate.

[0013] As used herein, the term “PDI” means polydispersity index, and is used synonymously with the term “MWD” (molecular weight distribution), which is characterized herein using Size-Exclusion Chromatography (SEC). Molecular weight, including weight-average molecular weight (Mw) and number-average molecular weight (Mn), are determined using a High Temperature Size Exclusion (SEC) Chromatograph (either from Waters Corporation or Polymer Laboratories), equipped with a differential refractive index detector (DRI), an online light scattering detector, and a viscometer. Experimental details not described below, including how the detectors may be calibrated, are described in: *T. Sun, P. Brant, R. R. Chance, and W. W. Graessley*, 34(19) *MACROMOLECULES* 6812-6820 (2001). This is described further herein.

[0014] As part of the SEC (size exclusion chromatography) measurements for molecular weight distribution, values for “CLMS” and “CHMS” are obtained to further characterize the bimodal polymer, unimodal polymer and blend of the invention. CLMS is the weight % of polyethylene fractions under 1,000 amu, and CHMS is the weight % of the fraction of polyethylene fractions over 500,000 amu, the weight percent relative to the total composition; for example, if the “high density multimodal polyethylene composition” is being described, the weight % is that relative to the whole composition.

[0015] The term “multimodal polyethylene composition” as used herein, means a composition that includes at least a bimodal polyethylene (or multimodal polyethylene), but the meaning of the term also encompasses a composition that is preferred herein, which is a blend of a bimodal polyethylene and a unimodal polyethylene.

[0016] The term “bimodal,” when used herein to describe a polymer or polymer composition, e.g., polyethylene, means “bimodal molecular weight distribution,” which term is understood as having the broadest definition persons in the pertinent art have given that term as reflected in printed publications and issued patents. For example, a single composition that includes polyolefins with at least one identifiable high molecular weight component and polyolefins with at least one identifiable low molecular weight component is considered to be a “bimodal” polyolefin, as that term is used herein. Preferably, other than having different molecular weights, the high molecular weight polyolefin and the low molecular weight polyolefin are both polyethylenes but may have different levels of comonomer distribution. A material with more than two different molecular weight distributions (sometimes referred to as a “multimodal” polymer) will be considered “bimodal” as that term is used herein.

[0017] The term “unimodal,” as used herein to describe a polymer or polymer composition, means any polymer, e.g., polyethylene, that is not bimodal as defined above, e.g., one having a single molecular weight distribution.

5 [0018] The term “dual catalyst system” is intended to include a bimetallic catalyst as well as a multiple-catalyst system, and includes any composition, mixture or system that includes at least two different catalyst compounds, each having a different metal group. Preferably, each different catalyst compound resides on a single support particle, so that the dual or bimetallic catalyst is a supported dual or bimetallic catalyst. However, as used herein, the term bimetallic catalyst also broadly includes a system or mixture in which one of the catalysts resides on one
10 collection of support particles, and another catalyst resides on another collection of support particles. Preferably, in that latter instance, the two supported catalysts are introduced to a single reactor, either simultaneously or sequentially, and polymerization is conducted in the presence of the dual or bimetallic catalyst system, i.e., the two collections of supported catalysts.

15 [0019] The “high density multimodal polyethylene composition” or “composition” can be characterized by a number of properties, or any combination thereof, as described herein.

[0020] The TD Elmendorf Tear and MD Elmendorf Tear values refer to properties of a composition, or a polymer, or a film made of the polymer or composition being measured, and are measured according to ASTM D-1922-03. (The MD values refer to the machine direction
20 while the TD values refer to the transverse direction.)

[0021] The term “FI” as used herein means I_{21} , which is measured in accordance with ASTM-1238, Condition E, at 190 °C (21.6 kg).

[0022] The term “MFR (I_{21}/I_2)” as used herein means the ratio of I_{21} (also referred to as FI) to I_2 , and both I_{21} and I_2 are measured in accordance with ASTM-1238, Condition E, at 190 °C
25 (2.16 kg).

[0023] Various specific embodiments are described below, at least some of which are also recited in the claims.

[0024] For example, at least one specific embodiment is directed to a high density multimodal polyethylene composition, that has a density of 0.935 g/cc or more, and that

includes a blend of a first polyethylene component and a second polyethylene component, in which: the first polyethylene component includes a bimodal polyethylene; and the second polyethylene component includes a unimodal polyethylene that is made from a polymerization conducted in the presence of a metallocene having two cyclopentadienyl rings.

5 [0025] At least one other specific embodiment is directed to a high density multimodal polyethylene composition, that has a density of 0.935 g/cc or more, and that includes a blend of a first polyethylene component and a second polyethylene component, in which: the first polyethylene component includes a bimodal polyethylene; and the second polyethylene component includes a unimodal polyethylene that is made from a polymerization conducted in
10 the presence of a metallocene having two cyclopentadienyl rings.

[0026] Yet another other specific embodiment is directed to a high density multimodal polyethylene composition that has a density of 0.935 g/cc or more, and that includes a blend of a first polyethylene component and a second polyethylene component, in which: the first polyethylene component includes a bimodal polyethylene that includes a high molecular
15 weight component and a lower molecular weight component, the bimodal polyethylene being made from a polymerization conducted in the presence of a catalyst system that includes bis(2-(trimethylphenylamido)ethyl)amine zirconium dibenzyl and bis(n-propyl Cp) zirconium dichloride or difluoride; and the second polyethylene component includes a unimodal polyethylene that is made from a polymerization conducted in the presence of metallocene.

20 [0027] The components can be "blended" or otherwise intimately mixed by any suitable means such as by melt extrusion in a screw extruder or Brabender-type blender or other melt blending processes, or by *in situ* reactor blending such as by reacting various catalyst components with suitable activators and olefins in one or more reactors to produce the blends of the invention.

25 [0028] Still another specific embodiment is directed to a high density multimodal polyethylene composition that has a density of 0.935 g/cc or more, and that includes a blend of a first polyethylene component and a second polyethylene component, in which: the first polyethylene component includes a bimodal polyethylene that includes a high molecular weight component and a lower molecular weight component, the bimodal polyethylene being
30 made from a polymerization conducted in the presence of a dual catalyst system that includes metallocene; the second polyethylene component includes a unimodal polyethylene that is

made from a polymerization conducted in the presence of metallocene; and the multimodal polyethylene composition has an Elmendorf Tear ratio (TD/MD) of less than 8, based on a 1.0 mil film made from the composition.

[0029] In one embodiment, the metallocene used to make the unimodal polyethylene includes zirconium. In another embodiment the metallocene used to make the unimodal polyethylene includes a methyl group. In yet another embodiment the metallocene used to make the unimodal polyethylene includes a butyl group. In yet a more preferred embodiment, the metallocene used to make the unimodal polyethylene is bis(1,3-methylbutylcyclopentadienyl) zirconium dichloride or difluoride.

10 [0030] In one embodiment, the unimodal polyethylene comprises less than 20 wt% of the composition, and comprises less than 15 wt% of the composition in a preferred embodiment, and comprises less than 10 wt% of the composition in a most preferred embodiment.

15 [0031] In one embodiment, the Elmendorf Tear ratio (TD/MD) of the composition is 10 or less, based on a 1.0 mil film made from the composition, and is less than 8, based on a 1.0 mil film made from the composition in a more preferred embodiment, and is less than 5, based on a 1.0 mil film made from the composition in a most preferred embodiment.

[0032] In one embodiment, the Elmendorf Tear ratio (TD/MD) of the composition is less than 8, based on a 0.5 mil film made from the composition.

20 [0033] In one embodiment, the MD Elmendorf Tear of the composition is 50 grams or more, based on 1.0 mil film made from the composition, and is 100 grams or more, based on 1.0 mil film made from the composition in a preferred embodiment, and is 130 grams or more, based on 1.0 mil film made from the composition in yet a most preferred embodiment.

25 [0034] In one embodiment, the MD Elmendorf Tear of the composition is 10 grams or more, based on 0.5 mil film made from the composition, and is 15 grams or more, based on 0.5 mil film made from the composition in a more preferred embodiment.

[0035] In one embodiment, the TD Elmendorf Tear of the composition is 180 grams or more, based on 1.0 mil film made from the composition, and is 400 grams or more, based on 1.0 mil film made from the composition in a preferred embodiment, and is 500 grams or more, based on 1.0 mil film made from the composition in a most preferred embodiment.

[0036] In one embodiment, the TD Elmendorf Tear of the composition is 20 grams or more, based on 0.5 mil film made from the composition, and is 60 grams or more, based on 0.5 mil film made from the composition in a preferred embodiment, and is 100 grams or more, based on 0.5 mil film made from the composition in a most preferred embodiment.

5 [0037] In one embodiment, the MFR (I_{21}/I_2) of the composition is 50 or 60 or 70 to 150 or 200 or 250.

[0038] In one embodiment, the FI of the composition is 4 or 5 or 6 to 10 or 15 or 20.

[0039] In one embodiment, the density of the composition is 0.935 or 0.940 to 0.955 or 0.960 g/cc.

10 [0040] In one embodiment, the PDI of the composition is 30 or 40 to 60 or 65 or 70.

[0041] In one or more of the compositions identified above, or elsewhere herein, the bimodal polyethylene can have different characteristics and/or properties, and the bimodal polyethylene can be prepared using different catalyst systems.

[0042] As discussed below and elsewhere herein, a composition that includes a
15 metallocene-catalyzed unimodal polyethylene is described. Preferably, the unimodal polyethylene is a metallocene produced linear low density polyethylene as described in various embodiments herein. Catalyst systems that include a metallocene also comprise at least one activator, and optionally a support material such as an inorganic oxide support in one embodiment. Suitable activators such as aluminoxanes and tris(perfluorophenyl)borates are
20 well known in the art.

[0043] Metallocene catalyst compounds are described in general in 1 & 2 METALLOCENE-BASED POLYOLEFINS (John Scheirs & W. Kaminsky eds., John Wiley & Sons, Ltd. 2000); G.G. Hlatky in 181 Coordination Chem. Rev. 243-296 (1999) and in particular, those metallocenes for use in the synthesis of polyethylene in 1 METALLOCENE-BASED POLYOLEFINS 261-377
25 (2000). The metallocene catalyst compounds described herein include "half sandwich" and "full sandwich" compounds having one or more Cp ligands (cyclopentadienyl and ligands isolobal to cyclopentadienyl) bound to at least one Group 3 to Group 12 metal atom, and one or more leaving group(s) bound to the at least one metal atom. Hereinafter, these compounds will be referred to as "metallocenes" or "metallocene catalyst components." Each metallocene

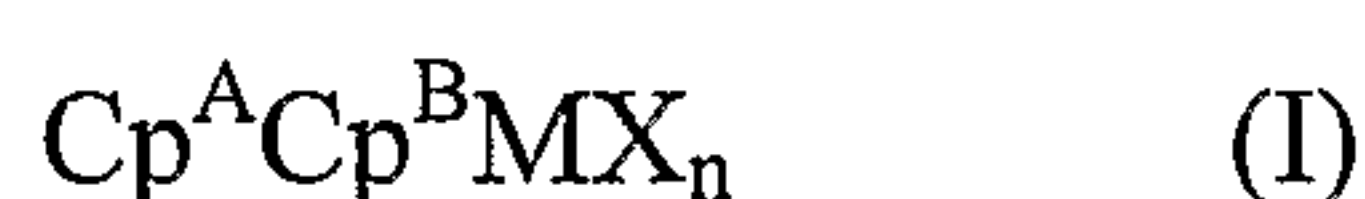
described herein is preferably supported on a support material in a particular embodiment when used to produce the unimodal polyethylenes of the invention, and may be supported with or without another catalyst component.

[0044] In at least one broad embodiment, the metallocene catalyst is a compound represented by the formula (I) below, wherein "Cp" refers to either a cyclopentadienyl ring, which may be substituted or unsubstituted, or a cyclopentadienyl ring derivative, such as an indenyl ring, which also may be substituted or unsubstituted. In a specific embodiment the metallocene used to make the unimodal polyethylene includes two cyclopentadienyl rings, and such a metallocene is referred to herein as a "biscyclopentadienyl metallocene" or a "bis-Cp metallocene." Preferably, the metallocene used to form one of the polyethylenes, and preferably the metallocene used to form (e.g., prepare or make) the "second polyethylene" described herein (e.g., one of the two polyethylenes in a 2-polyethylene blend composition) has two or more Cp ligands, most preferably two Cp ligands that are unbridged; and is thus to be considered a "bis-Cp metallocene." In a more specific embodiment, the metallocene is a substituted biscyclopentadienyl, preferably one that is substituted with a methyl group and a butyl group, such as bis(1,3-methylbutylcyclopentadienyl) zirconium dichloride or difluoride.

[0045] The Cp ligands are one or more rings or ring system(s), at least a portion of which includes π -bonded systems, such as cycloalkadienyl ligands and heterocyclic analogues. The ring(s) or ring system(s) typically comprise atoms selected from the group consisting of Groups 13 to 16 atoms, and more particularly, the atoms that make up the Cp ligands are preferably selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum and combinations thereof, wherein carbon makes up at least 50% of the ring members. Even more particularly, the Cp ligand(s) are preferably selected from the group consisting of substituted and unsubstituted cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, non-limiting examples of which include cyclopentadienyl, indenyl, fluorenyl and other structures. Further non-limiting examples of such ligands include cyclopentadienyl, cyclopentaphenanthrenyl, indenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated versions thereof (e.g., 4,5,6,7-tetrahydroindenyl, or "H₄Ind"), substituted versions thereof (as described in more detail below), and heterocyclic versions thereof.

[0046] The metal atom "M" of the metallocene catalyst compound, as described throughout the specification and claims, may be selected from the group consisting of Groups 4, 5 and 6 atoms one embodiment, and a Ti, Zr, Hf atoms in yet a more particular embodiment, and Zr in yet a more particular embodiment. The oxidation state of the metal atom "M" may range from 0 to +7 in one embodiment; and in a more particular embodiment, is +1, +2, +3, +4 or +5; and in yet a more particular embodiment is +2, +3 or +4. The groups bound the metal atom "M" are such that the compounds described below in the formulas and structures are electrically neutral, unless otherwise indicated. The Cp ligand(s) form at least one chemical bond with the metal atom M to form the "metallocene catalyst compound". The Cp ligands are distinct from the leaving groups bound to the catalyst compound in that they are not highly susceptible to substitution/abstraction reactions.

[0047] In one aspect of the invention, the metallocene catalyst described herein can be represented by the formula (I):



[0048] wherein M is as described above; each X is chemically bonded to M; each Cp group is chemically bonded to M; and n is 0 or an integer from 1 to 4, and either 1 or 2 in a particular embodiment.

[0049] The ligands represented by Cp^{A} and Cp^{B} in formula (I) may be the same or different cyclopentadienyl ligands or ligands isolobal to cyclopentadienyl, either or both of which may contain heteroatoms and either or both of which may be substituted by a group R. In one embodiment, Cp^{A} and Cp^{B} are independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, and substituted derivatives of each.

[0050] Independently, each Cp^{A} and Cp^{B} of formula (I) may be unsubstituted or substituted with any one or combination of substituent groups R. Non-limiting examples of substituent groups R as used in structure (I) as well as ring substituents in structures (Va-d) include groups selected from the group consisting of hydrogen radicals, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidols, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, and combinations thereof.

[0051] More particular non-limiting examples of alkyl substituents R associated with formula (I) through (V) include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl, phenyl, methylphenyl, and tert-butylphenyl groups and the like, including all their isomers, for example tertiary-butyl, isopropyl, and the like.

5 [0052] Each X in the formula (I) above and for the formulas (II) through (IV) below is independently selected from the group consisting of: any leaving group in one embodiment; halogen ions, hydrides, C₁ to C₁₂ alkyls, C₂ to C₁₂ alkenyls, C₆ to C₁₂ aryls, C₇ to C₂₀ alkylaryls, C₁ to C₁₂ alkoxys, C₆ to C₁₆ aryloxys, C₇ to C₁₈ alkylaryloxys, C₁ to C₁₂ fluoroalkyls, C₆ to C₁₂ fluoroaryls, and C₁ to C₁₂ heteroatom-containing hydrocarbons and substituted derivatives
 10 thereof in a more particular embodiment; chloride, fluoride, C₁ to C₆ alkyls, C₂ to C₆ alkenyls, C₇ to C₁₈ alkylaryls, halogenated C₁ to C₆ alkyls, halogenated C₂ to C₆ alkenyls, and halogenated C₇ to C₁₈ alkylaryls in yet a more particular embodiment; fluoride, methyl, ethyl, propyl, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, fluoromethyls (mono-, di- and trifluoromethyls) and fluorophenyls (mono-, di-, tri-, tetra- and pentafluorophenyls) in yet a
 15 more particular embodiment; and fluoride in yet a more particular embodiment.

[0053] In another aspect of the invention, the metallocene catalyst component includes those of formula (I) where Cp^A and Cp^B are bridged to each other by at least one bridging group, (A), such that the structure is represented by formula (II):



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[0054] These bridged compounds represented by formula (II) are known as “bridged metallocenes”. Cp^A, Cp^B, M, X and n in structure (II) are as defined above for formula (I); and wherein each Cp ligand is chemically bonded to M, and (A) is chemically bonded to each Cp. Non-limiting examples of bridging group (A) include divalent hydrocarbon groups containing
 25 at least one Group 13 to 16 atom, such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom and combinations thereof; wherein the heteroatom may also be C₁ to C₁₂ alkyl or aryl substituted to satisfy neutral valency. The bridging group (A) may also contain substituent groups R as defined above (for formula (I)) including halogen radicals and iron. More particular non-limiting examples of
 30 bridging group (A) are represented by C₁ to C₆ alkylenes, substituted C₁ to C₆ alkylenes, oxygen, sulfur, R'₂C=, R'₂Si=, -Si(R')₂Si(R')-, R'₂Ge=, R'P= (wherein “=” represents two chemical bonds), where R' is independently selected from the group consisting of hydride,

hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 atoms, substituted Group 16 atoms, and halogen radical; and wherein two or more R' may be joined to form a ring or ring system. In one embodiment, the bridged metallocene catalyst component of formula (II) has two or more bridging groups (A).

[0055] The ligands Cp^A and Cp^B of formulae (I) and (II) are different from each other in one embodiment, and the same in another embodiment.

[0056] In yet another aspect of the invention, the metallocene catalyst components include bridged mono-ligand metallocene compounds (e.g., mono cyclopentadienyl catalyst components). In this embodiment, the at least one metallocene catalyst component is a bridged "half-sandwich" metallocene as in, for example, US 5,055,438, represented by the formula (III):



[0057] wherein Cp^A is defined above and is bound to M; (A) is a bridging group bonded to Q and Cp^A ; and wherein an atom from the Q group is bonded to M; and n is 0 or an integer from 1 to 3; 1 or 2 in a particular embodiment. In formula (III) above, Cp^A , (A) and Q may form a fused ring system. The X groups and n of formula (III) are as defined above in formula (I) and (II). In one embodiment, Cp^A is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted versions thereof, and combinations thereof.

[0058] In formula (III), Q is a heteroatom-containing ligand in which the bonding atom (the atom that is bonded with the metal M) is selected from the group consisting of Group 15 atoms and Group 16 atoms in one embodiment, and selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur atom in a more particular embodiment, and nitrogen and oxygen in yet a more particular embodiment. Non-limiting examples of Q groups include alkylamines, arylamines, mercapto compounds, ethoxy compounds, carboxylates (e.g., pivalate), carbamates, azenyl, azulene, pentalene, phosphoyl, phosphinimine, pyrrolyl, pyrolyl, carbazoyl, borabenzene other compounds comprising Group 15 and Group 16 atoms capable of bonding with M.

[0059] In yet another aspect of the invention, the at least one metallocene catalyst component is an unbridged "half sandwich" metallocene represented by the formula (IVa):



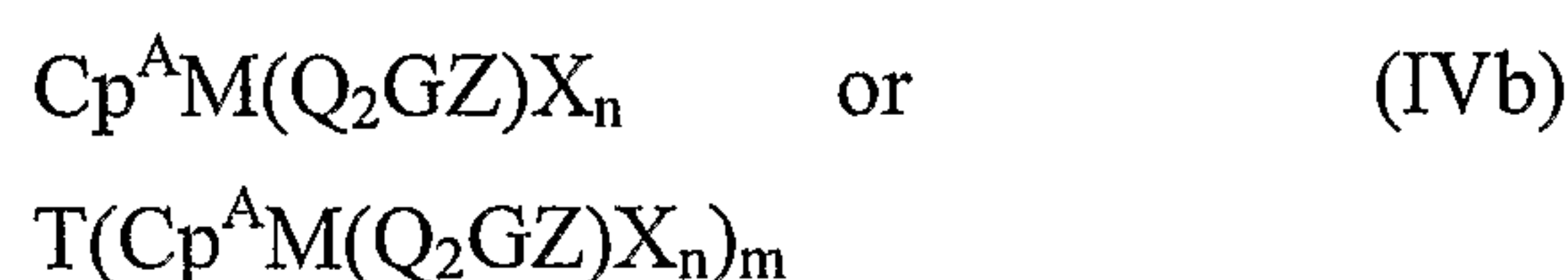
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[0060] wherein Cp^{A} is defined as for the Cp groups in (I) and is a ligand that is bonded to M; each Q is independently bonded to M; Q is also bound to Cp^{A} in one embodiment; X is a leaving group as described above in (I); n ranges from 0 to 3, and is 1 or 2 in one embodiment; q ranges from 0 to 3, and is 1 or 2 in one embodiment. In one embodiment, Cp^{A} is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted version thereof, and combinations thereof.

[0061] In formula (IVa), Q is selected from the group consisting of ROO^- , RO^- , $\text{R}(\text{O})^-$, $-\text{NR}-$, $-\text{CR}_2-$, $-\text{S}-$, $-\text{NR}_2$, $-\text{CR}_3$, $-\text{SR}$, $-\text{SiR}_3$, $-\text{PR}_2$, $-\text{H}$, and substituted and unsubstituted aryl groups, wherein R is selected from the group consisting of C_1 to C_6 alkyls, C_6 to C_{12} aryls, C_1 to C_6 alkylamines, C_6 to C_{12} alkylarylamines, C_1 to C_6 alkoxys, C_6 to C_{12} aryloxys, and the like. Non-limiting examples of Q include C_1 to C_{12} carbamates, C_1 to C_{12} carboxylates (e.g., pivalate), C_2 to C_{20} allyls, and C_2 to C_{20} heteroallyl moieties.

[0062] Described another way, the "half sandwich" metallocenes above can be described as in formula (IVb), such as described in, for example, US 6,069,213:

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[0063] wherein M, Cp^{A} , X and n are as defined above;

[0064] Q_2GZ forms a polydentate ligand unit (e.g., pivalate), wherein at least one of the Q groups form a bond with M, and is defined such that each Q is independently selected from the group consisting of $-\text{O}-$, $-\text{NR}-$, $-\text{CR}_2-$ and $-\text{S}-$; G is either carbon or silicon; and Z is selected from the group consisting of R, $-\text{OR}$, $-\text{NR}_2$, $-\text{CR}_3$, $-\text{SR}$, $-\text{SiR}_3$, $-\text{PR}_2$, and hydride, providing that when Q is $-\text{NR}-$, then Z is selected from the group consisting of $-\text{OR}$, $-\text{NR}_2$, $-\text{SR}$, $-\text{SiR}_3$, $-\text{PR}_2$; and provided that neutral valency for Q is satisfied by Z; and wherein each R

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is independently selected from the group consisting of C₁ to C₁₀ heteroatom containing groups, C₁ to C₁₀ alkyls, C₆ to C₁₂ aryls, C₆ to C₁₂ alkylaryls, C₁ to C₁₀ alkoxys, and C₆ to C₁₂ aryloxys;

[0065] n is 1 or 2 in a particular embodiment; and

5 [0066] T is a bridging group selected from the group consisting of C₁ to C₁₀ alkenes, C₆ to C₁₂ aryls and C₁ to C₁₀ heteroatom containing groups, and C₆ to C₁₂ heterocyclic groups; wherein each T group bridges adjacent "Cp^AM(Q₂GZ)X_n" groups, and is chemically bonded to the Cp^A groups.

[0067] m is an integer from 1 to 7; m is an integer from 2 to 6 in a more particular embodiment.

10 [0068] As used herein, a single, bridged, asymmetrically substituted metallocene catalyst component having a racemic and/or meso isomer does not, itself, constitute at least two different bridged, metallocene catalyst components. In a preferred embodiment, the metallocenes described herein are in their racemic form.

15 [0069] The "metallocene catalyst component" useful in the present invention may comprise any combination of any "embodiment" described herein. The bimetallic catalyst system useful in producing the bimodal polyethylenes described herein, preferably includes one metallocene, most preferably an unbridged bis-Cp metallocene.

[0070] In one embodiment of the second polyethylene component, or unimodal polyethylene, is a linear low density polyethylene having a density of from 0.88 to 0.93 g/cc, and in a more preferred embodiment a density of from 0.90 to 0.925 g/cc, and from 0.91 to 0.92 in yet a more preferred embodiment, wherein a desirable density range may comprise any upper limit with any lower limit described herein. In another embodiment, the unimodal polyethylene has a weight average molecular weight of from 2,000 to 200,000 amu in one embodiment, and from 4,000 to 120,000 amu in another embodiment, and from 10,000 to 120,000 amu in yet a more preferred embodiment; and a z-average molecular weight of from less than 300,000 amu in one embodiment, and from less than 280,000 amu in another embodiment, and from less than 250,000 amu in yet another embodiment; and a molecular weight distribution (PDI) from less than 4.2 in one embodiment, and less than 4.0 in a more preferred embodiment, and from less than 3.8 in yet another embodiment, and from less than 3.5 in yet a more preferred embodiment. In yet another embodiment the unimodal

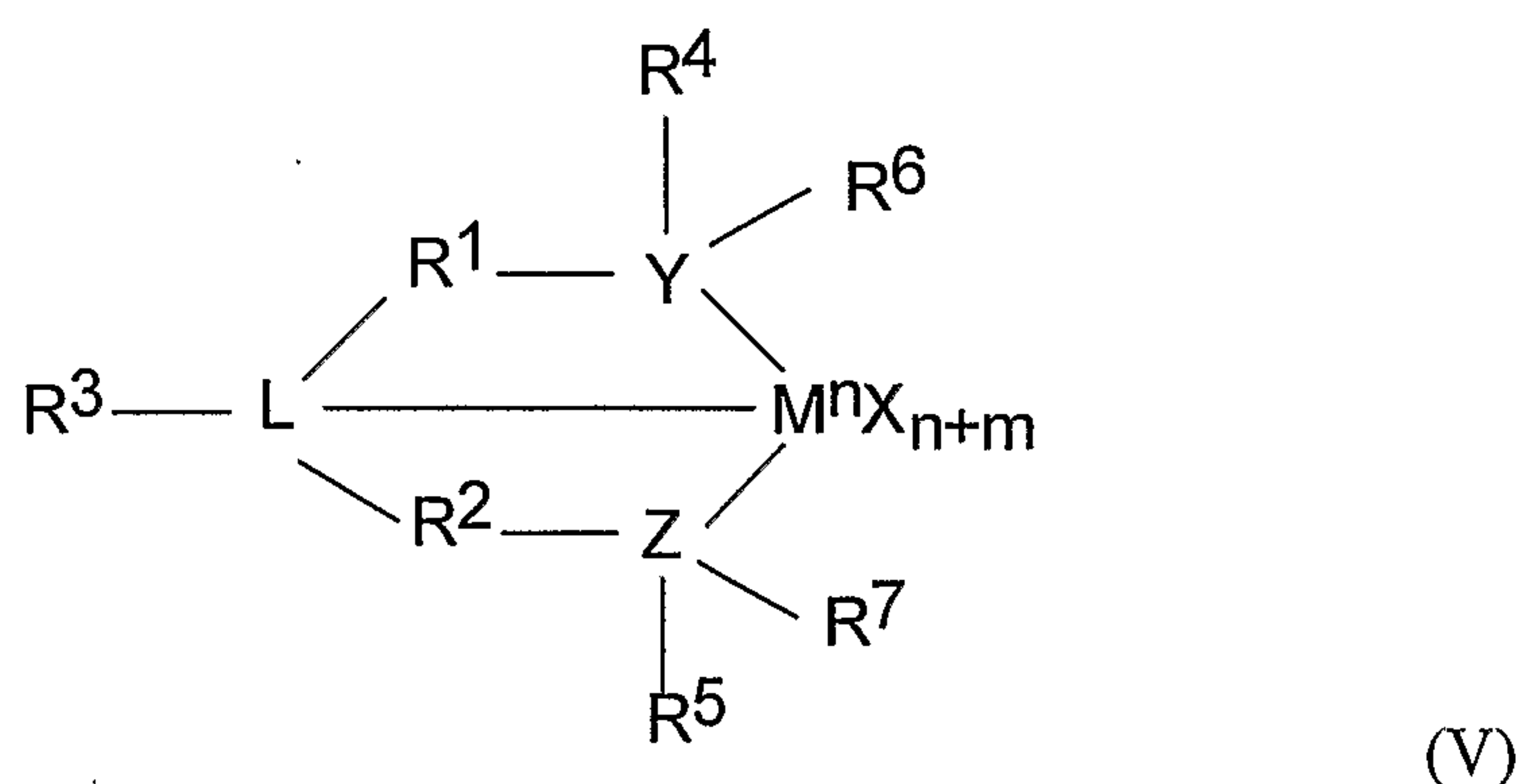
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polyethylene has a MI (I_2 , 2.16kg/190°C) of from 0.2 to 100 dg/min, and more preferably from 0.5 to 20 dg/min, and more preferably from 0.6 to 10, and even more preferably from 0.8 to 2 dg/min, wherein a desirable melt index comprises any combination of any upper limit with any lower limit described herein.

- 5 [0071] One or more specific embodiments of the compositions described herein include a bimodal polyethylene. In certain embodiments, a bimodal polyethylene for the composition may be prepared as described in U.S. Patent Nos. 6,605,675 or 6,608,149. In at least one particular embodiment, a composition includes a bimodal polyethylene prepared using dual catalyst systems described below.
- 10 [0072] For example, a bimodal polyethylene can be prepared by a polymerization conducted in the presence of a catalyst system that includes a fumed particulate filler, an activator, a metallocene and a catalyst compound represented by the formula (V):



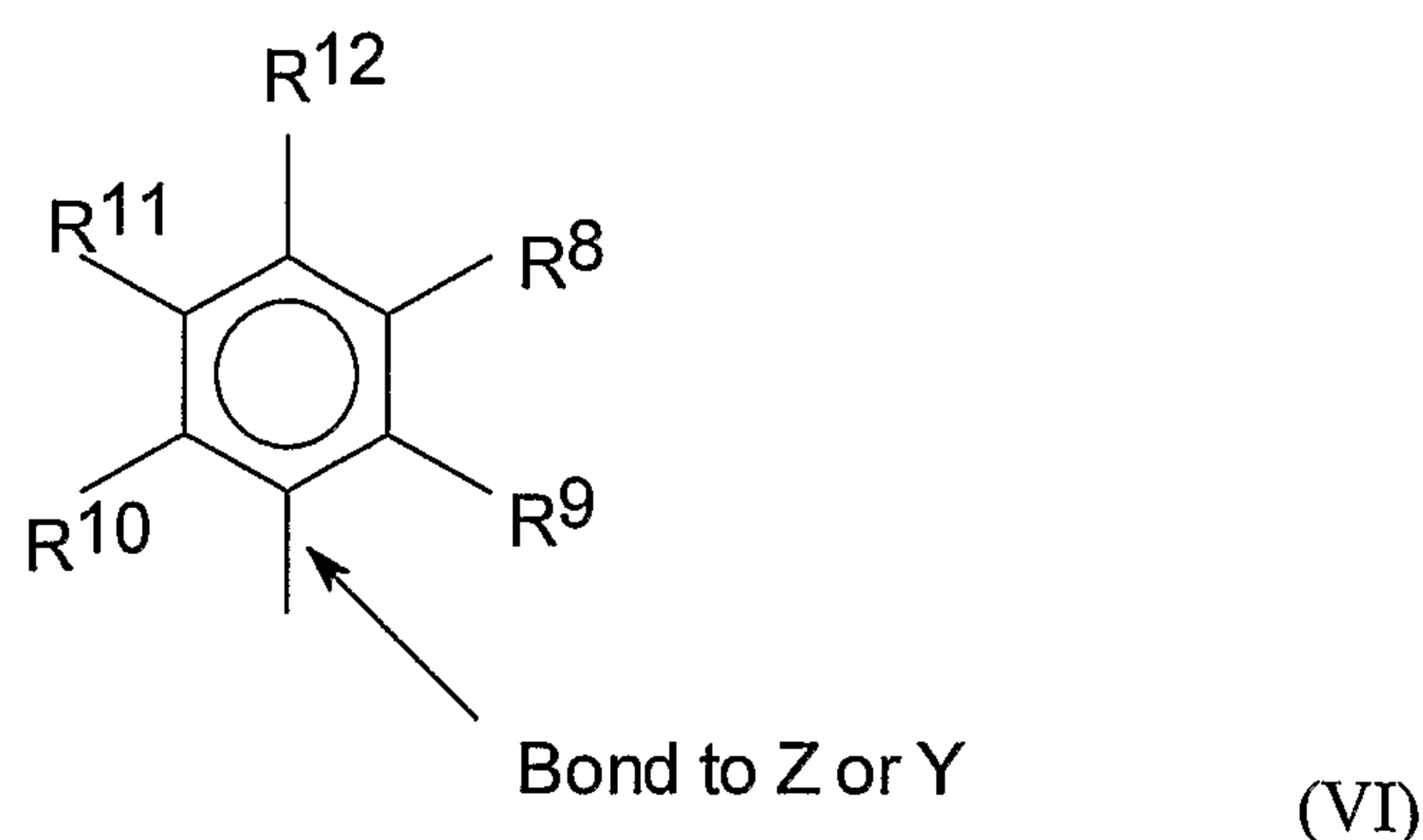
- 15 [0073] wherein M is a Group 4, 5 or 6 metal; each X is independently an anionic leaving group; n is the oxidation state of M; m is the formal charge of the ligand comprising Y, Z and L; Y is a Group 15 atom; Z is a Group 15 atom; L is a Group 15 atom; R^1 and R^2 are independently a C_1 to C_{20} hydrocarbon group, or a heteroatom containing group wherein the heteroatom is silicon, germanium, tin, lead, or phosphorus; optionally, R^1 and R^2 are interconnected to each other; R^3 is absent, a hydrogen, a group 14 atom containing group, a halogen, or a heteroatom containing group; R^4 and R^5 are independently an alkyl group, an aryl group, a substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, or a multiple ring system; and R^6 and R^7 are independently absent, a hydrogen, an alkyl group, a halogen, a heteroatom, a hydrocarbyl group, or a heteroatom containing group.
- 20

[0074] Catalyst systems suitable for producing the bimodal polyethylenes of the invention also include at least one activator, and optionally a support material such as an inorganic oxide support, preferably having an average particle size of from less than 50 μm , and most preferably less than 2 μm . Suitable activators such as aluminoxanes and tris(perfluorophenyl)borates are well known in the art. The catalyst system suitable for producing the bimodal polyethylenes also preferably include a metallocene compound as described generally above.

[0075] In one or more specific embodiments, referring to the catalyst formula (V), M can be zirconium or hafnium. In one or more specific embodiments, referring to the catalyst formula above, each X may be independently a hydrogen, a halogen or a hydrocarbyl group. In one or more specific embodiments, referring to the catalyst formula above, R^1 and R^2 can be independently a C_2 to C_6 hydrocarbon group. In one or more specific embodiments, referring to the catalyst formula above, R^1 and R^2 can be a C_1 to C_{20} alkylene, C_5 to C_{20} arylene or C_5 to C_{20} arylalkylene group. In one or more specific embodiments, referring to the catalyst formula above, m can be 0, -1, -2, or -3 and n is +3, +4 or +5. In one or more specific embodiments, referring to the catalyst formula above, R^3 can be hydrogen or a methyl group.

[0076] In one or more specific embodiments, referring to the catalyst formula (V), R^4 and R^5 can be independently an alkyl group, an aryl group, a substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, or a multiple ring system having up to 20 carbon atoms.

[0077] In one or more specific embodiments, referring to the catalyst formula (V), R^4 and R^5 are independently a group represented by the following formula:



[0078] wherein each R^8 to R^{12} are independently hydrogen, a C_1 to C_{20} alkyl group, a heteroatom, or a heteroatom containing group having up to 40 carbon atoms, and any two R^{8-12} groups can combine to form a cyclic group or a heterocyclic group.

5 [0079] In one or more specific embodiments, referring to the catalyst formula (VI), R^9 , R^{10} and R^{12} are methyl and R^8 and R^{11} are hydrogen.

[0080] In one or more specific embodiments, referring to the catalyst formula above, the catalyst system further includes mineral oil.

[0081] In one or more specific embodiments, referring to the catalyst formula above, the catalyst system is a slurry of solids, the solids concentration ranging from 10 to 15 wt%.

10 [0082] In one or more specific embodiments, referring to the catalyst formula above, the catalyst system has a particle size up to 25 μm .

[0083] In one or more specific embodiments, referring to the catalyst formula above, the catalyst system includes a particulate filler having an average particle size of 0.001 μm to 1 μm .

15 [0084] In one or more specific embodiments, referring to the catalyst formula above, the catalyst system includes a particulate filler that has been treated with dimethylsilyldichloride.

[0085] In one or more specific embodiments, referring to the catalyst formula above, the bimodal polyethylene can be made by a polymerization conducted in the presence of a catalyst system that includes a slurry of mineral oil, particulate filler, a metallocene catalyst compound, and a catalyst compound represented by the formula (V).

20 [0086] In one or more specific embodiments the metallocene compound that is part of the dual catalyst is a bridged or unbridged zirconocene or hafnocene metallocene compound.

25 [0087] In one or more specific embodiments, referring to the catalyst formula (V), the particulate filler comprises silica, the activator comprises an alumoxane; wherein the silica comprises from 50 to 60 wt% of the dried support, catalyst compound and activator composition.

[0088] In one or more specific embodiments, referring to the catalyst formula (V), the activator, particulate filler and at least one catalyst compound are spray-dried.

[0089] In one embodiment, the bimodal polyethylene useful in blends of the present invention possesses an MI (I_2) of less than 1 dg/min, and more preferably less than 0.1 dg/min; and possesses an FI (I_{21}) value of from 1 to 20 dg/min, and from 2 to 16 dg/min in another embodiment, and from 3 to 12 in yet a more preferred embodiment; and an MFR (I_{21}/I_2) of
5 from 30 to 200 in one embodiment, and more preferably from 40 to 180, and even more preferably from 60 to 140; and a molecular weight distribution (PDI) of from 10 to 100 in one embodiment, and more preferably from 20 to 80, and even more preferably from 30 to 60; and a weight average molecular weight of from 50,000 to 400,000 amu in one embodiment, and from 60,000 to 300,000 amu in a more preferred embodiment; and a density of from 0.93 to
10 0.98 g/cc in one embodiment, and from 0.935 to 0.97 g/cc in another embodiment, and from 0.94 to 0.96 g/cc in yet another embodiment. The bimodal polyethylenes useful in the present invention, when produced by the preferred catalyst composition described above, may possess these properties, as well as a CLMS value of from less than 10 wt%, and from less than 6 wt% in a preferred embodiment; and a CHMS value of from less than 24 wt% in one embodiment,
15 and from less than 20 wt% in a preferred embodiment.

[0090] The unimodal and bimodal polyethylenes described herein can be produced by any suitable polymerization process known to polymerize olefins into polyolefins; such processes include solution, slurry, and gas phase processes, both low pressure and so called high pressure processes, as well as single or dual-reactor processes, the later of which includes the use of two
20 or more reactors in series. In one embodiment, the bimodal polyethylene is produced in a single reactor gas phase process.

[0091] The unimodal and bimodal polyethylenes described herein can be "blended" by any suitable technique to achieve the features of the high density multimodal polyethylene composition as described and claimed herein. In a preferred embodiment, the components are
25 melt extruded in a screw-type extruder, as is well known in the art.

[0092] The high density multimodal polyethylene compositions resulting from the blending of the unimodal and bimodal polyethylenes can be described by any combination of features as disclosed herein. In a preferred embodiment, the compositions possess a density of from at least 0.935 g/cc, and from 0.935 to 0.97 g/cc in another embodiment, and most preferably a
30 density of from 0.935 to 0.95 g/cc; and an I_{21} value of from 1 to 20 dg/min in one embodiment, and most preferably from 3 to 10 dg/min; and an MFR (I_{21}/I_2) of from 30 or 40 to 70 or 160, and most preferably from 60 to 120; and a z-average molecular weight of from 900,000 to

1,600,000 amu in one embodiment, and most preferably from 1,000,000 to 1,500,000 amu. The high density multimodal polyethylene compositions also possess a CLMS value of from less than 10 wt% in one embodiment, and from less than 6 wt% in a preferred embodiment; and a CHMS value of from less than 24 wt% in one embodiment, and from less than 20 wt% in a preferred embodiment, and less than 16 wt% in a most preferred embodiment. Other features of the high density multimodal polyethylene composition are as described and claimed herein.

EXAMPLES

[0093] The following examples discuss different polyethylene resins, different compositions, and films made from such compositions.

10 [0094] The PDI ("MWD"), CHMS, CLMS and other molecular weight determinations were performed as follows. Three Polymer Laboratories PLgel 10mm Mixed-B columns were used. The nominal flow rate was 0.5 cm³/min, and the nominal injection volume was 300 microliters. The various transfer lines, columns and differential refractometer (the DRI detector) are contained in an oven maintained at 135°C.

15 [0095] Solvent for the SEC experiment (described in the examples) was prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of Aldrich reagent grade 1,2,4-trichlorobenzene (TCB). The TCB mixture was then filtered through a 0.7 micrometers glass pre-filter and subsequently through a 0.1 micrometers Teflon filter. The TCB was then degassed with an online degasser before entering the SEC columns.

20 [0096] Polymer solutions were prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160 °C with continuous agitation for about 2 hours. All quantities were measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/ml at room temperature and 1.324 g/ml at 135 °C. The injection concentration ranged from 1.0 to 2.0
25 mg/ml, with lower concentrations being used for higher molecular weight samples.

[0097] Prior to running each sample the DRI detector and the injector was purged. Flow rate in the apparatus was then be increased to 0.5 ml/minute, and the DRI be allowed to stabilize for 8-9 hours before injecting the first sample. The LS laser should be turned on 1 to 1.5 hours before running samples by running the laser in idle mode for 20-30 minutes and then

switching to full power in light regulation mode. Depending on the specific instrument used, data can be collected at a rate of 0.5 to 4.0 seconds for each "slice" (point.)

[0098] The concentration, "c", at each point in the chromatogram was calculated from the DRI output, i.e., the baseline-subtracted DRI signal, I_{DRI} , using the following Equation 1 :

5 Equation 1: $c = K_{DRI} I_{DRI} / (dn/dc)$

where K_{DRI} is a constant determined by calibrating the DRI, and (dn/dc) is the same as described below for the LS analysis. Units on parameters throughout this description of the SEC method are such that concentration is expressed in g/cm^3 , molecular weight is expressed
10 in g/mole, and intrinsic viscosity is expressed in dL/g.

[0099] The light scattering detector used was either a Wyatt Technology High Temperature mini-DAWN or a Precision Detector 2040 LALLS. The data was analyzed with the standard formula for static light scattering, i.e. Equation 2:

Equation 2:
$$\frac{K_0 c}{\Delta R(\theta, c)} = \frac{1}{MP(\theta)} + 2A_2 c$$

15 where $\Delta R(\theta, c)$ is the excess Rayleigh scattering intensity at scattering angle θ , c is the polymer concentration, M is the polymer molecular weight, A_2 is the second virial coefficient of the solution, $P(\theta)$ is the form factor, and K_0 is the optical constant for the system:

Equation 3:
$$K_0 = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

20 in which N_A is Avogadro's number, and dn/dc is the refractive index increment for the system. For the LALLS detector the scattering intensity is preferably measured at 15° and $P(\theta)=1$ is assumed. The concentrations used in the analyses were the values obtained from the DRI output. The refractive index n for TCB at 135 C for a 690 nm wavelength is 1.500. The value
25 $A_2 = 0.0015 \text{ mole}\cdot\text{ml}/\text{gm}^2$ is used for ethylene-hexene and ethylene-butene polymers with less

than 15 weight% comonomer. The value $(dn/dc) = 0.104$ is used for polyethylene and ethylene-hexene copolymers and the value $(dn/dc) = 0.104 \times (1 - 0.126w)$ is used for ethylene-butene copolymers where “w” is the weight fraction of butane-derived units.

5 [00100] The viscometer that was used is a Viscotek Corporation high temperature viscometer that has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers. The first transducer should measure the total pressure drop across the detector, and the other transducer, positioned between the two sides of the bridge, was used to measure a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation, where “c” was determined from the DRI output:

Equation 4:
$$\eta_s = c[\eta] + 0.3(c[\eta])^2$$

Example 1

15 [00101] This example discusses the preparation and physical properties of a bimodal polyethylene and two different types of unimodal polyethylene resins. See Table 1. The Sample 1 bimodal polyethylene was prepared in a single gas phase reactor, in the presence of a mixed catalyst system that included bis(2-(trimethylphenylamido)ethyl)amine zirconium dibenzyl, for generating the higher molecular weight component of the bimodal polyethylene composition, and bis(n-propylcyclopentadienyl) zirconium dichloride, for generating the lower molecular weight component of the bimodal polyethylene composition. The Sample 2 unimodal resin was a linear low density polyethylene (LLDPE) made from a bis(1,3-methylbutylcyclopentadienyl) zirconium dichloride metallocene catalyst having the characteristics outlined in Table 1. The Sample 3 unimodal resin was ST 2005, a linear low density polyethylene (LLDPE) resin composition sold commercially by Dow Chemical Co., also called “Super Tuflin,” produced by UCAT A, which is a Ziegler-Natta catalyst having the characteristics outlined in Table 1.

Table 1

	Sample 1 (Sample 4) "bimodal"	Sample 2 "MCN" LLDPE	Sample 3 "ZN" LLDPE
Resin Properties:			
MI (I ₂)	0.059 (0.062)	0.989	0.888
FI (I ₂₁)	6.87 (7.21)	15.66	22.13
MFR (I ₂₁ /I ₂)	116 (116)	15.8	24.9
Density (g/cc)	0.9491 (0.9536)	0.9181	0.9153
<u>SEC data:</u>			
Mn	NA (4,654)	47,616	25,838
Mw	NA (256,250)	118,847	123,498
Mw/Mn	NA (55.1)	2.49	4.78
Mz	NA (1,143,034)	212,129	348,074
CLMS (%)	NA (4.18)	-	0.15
CHMS (%)	NA (15.3)	1.02	3.59

Example 2

5 **[00102]** This example discusses the blend compositions prepared using the Sample 1 bimodal resin together with Samples 2 or 3 unimodal resins, all described in Example 1. Up to 20 wt% of each unimodal resin was added to the bimodal resin, by dry blending and then melt compounding.

10 **[00103]** To make blends, pellets of the different resins were mixed in a tumble mixer at predetermined blend ratios. Each pellet mixture was compounded on a single screw Prodex pelletizer. The Sample 1 bimodal resin was re-compounded on the same extruder (pelletizer) to maintain the same melt shear history as that of the blends described below. Accordingly, referring to Table 1, the parenthetical values for Sample 1 represent properties of the re-compounded version of Sample 1, referred to herein as Sample 4.

[00104] Table 2 discloses resin property details for each blend, including the re-compounded bimodal resin (Sample 4). Samples 5, 6 and 7 are compositions that include Sample 1 resin blended with varying amounts (10 wt%, 15 wt% and 20 wt%) of the Sample 3 unimodal resin (ST 2005, "ZN"). Samples 8, 9 and 10 are compositions that include Sample 1 resin blended with varying amounts (10 wt%, 15 wt% and 20 wt%) of the Sample 2 unimodal resin (metallocene LLDPE, "MCN").

[00105] It was observed that both MI and FI of the blends increased as the wt % of each unimodal resin increased. In contrast, the MFR of the blends tended to show a decreasing trend as the wt % of each unimodal resin increased. The density of the blends dropped with the addition of unimodal resin. Table 3 indicates molecular information for the same compositions characterized in Table 2. Polydispersity (M_w/M_n) was observed to decrease as the percentage of unimodal polyethylene in the composition increased.

Table 2

	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
LLDPE	none	ZN	ZN	ZN	MCN	MCN	MCN
Wt. % of LLDPE (Samples 2 or 3)	0	10	15	20	10	15	20
MI (I_2)	0.062	0.081	0.086	0.108	0.087	0.097	0.111
FI (I_{21})	7.21	8.43	9.27	9.50	7.89	7.98	8.33
MFR (I_{21}/I_2)	116.1	104.6	107.8	87.9	92.9	85.7	76.5
Density (g/cc)	0.9536	0.9467	0.9453	0.9435	0.9448	0.9448	0.9433

Table 3

	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Mn	4,654	4,946	6,047	6,234	6,517	5,534	5,979
Mw	256,250	265,348	261,712	237,250	257,281	266,176	247,460
Mw/Mn	55.1	53.65	43.3	38.1	39.5	48.1	41.4
Mz	1,143,034	1,214,098	1,234,718	1,112,840	1,154,011	1,221,539	1,174,441
CLMS (%)	4.18	3.99	3.17	3.10	2.91	3.37	3.27
CHMS (%)	15.3	15.37	14.23	13.01	14.17	14.76	13.29

Example 3

[00106] This example discusses preparation of films from the various resin compositions described above. Both the resin blends and the re-compounded bimodal resin (Sample 4) were film extruded on the Alpine film extrusion line, which was equipped with a 50 mm, 18:1 L/D screw, 100 mm annular die (1 mm die gap). The temperature profile (degrees F) was set at 390/400/400/400/410/410/410/410 for Zones 1/2/3/4/5/6/7/8. Zones 1 and 2 are for screws. Zones 3, 4 and 5 are for adapter block. Zones 6, 7 and 8 are for die. Blow-up ratio (diameter of blown bubble divided by die diameter) was maintained at 4.0 throughout the runs. The take-up speed was 92 fpm and 184 fpm respectively, for 1.0 mil and 0.5 mil films. Cooling air flow rate was adjusted to maintain the frost line height ratio at 9.0. The frost line height ratio is a ratio between the height of frost line and the die diameter. At a constant output rate, the extrusion head pressure decreased as the blend ratio of unimodal resin increases while the motor load slightly decreased or remained the same. The decreasing effect was more prominent for ST2005 than for Sample 2 resin. The bubble stability of all the blends (up to 20% of unimodal resin) was good, producing 0.5 mil film without any difficulties. The film appearance rate of the blends was good (+40) with no gels or melt fracture appearing. The film surface showed no sign of poor homogeneity. Table 4 summarizes the film extrusion conditions. Further, it was noted that overall film extrudability of the blends was also improved with less motor load and extrusion head pressure without losing any bubble stability.

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Table 4

	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Die set temp. (°F)	410	410	410	410	410	410	410
Screw RPM	93	93	93	93	93	93	93
Screw amps.	62	61	61	59	62	62	62
Head pressure (psi)	8,500	8,250	8,050	7,800	8,350	8,150	8,000
Rate (lb/hr)	95	96	95	93	96	97	96
FAR	+40	+40	+40	+40	+40	+40	+40
BUR	4	4	4	4	4	4	4
Bubble stability	Good	Good	Good	Good	Good	Good	Good
Gels	No	No	No	No	No	No	No
FHR* (Frost-line Height/Die Diameter)	9	9	9	9	9	9	9

Example 5

5 [00107] This example discusses properties of the films. Surprisingly, the Elmendorf Tear
 results depended on which unimodal resin was used. Blends with Sample 2 resin exhibited not
 only enhanced MD and TD film tear but also a more balanced TD/MD tear ratio for both 1.0
 and 0.5 mil films. For blends having 10% and 15% of m-LLDPE, the TD/MD tear ratio for 1.0
 mil film was reduced to 3.8 and 3.7, respectively, from 10.6. For 0.5 mil film the TD/MD
 10 ratio reduced to 2.0 and 4.5, respectively, from 7.8. In contrast, blends that included ST2005
 showed little impact on MD tear for both 1.0 and 0.5 mil film. The TD tear seemed to increase
 a little as the wt % of that particular unimodal resin increased. As reflected in Table 5, film
 puncture resistance also increased in proportion to increased amounts of the Sample 2
 unimodal polyethylene in the composition.

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Table 5

	Film gauge (mil)	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Dart impact strength (g)	1.0	160	125	135	125	230	130	185
	0.5	320	170	160	133	220	170	160
Tensile strength @peak, psi (MD/TD)	1.0	10,800/7,700	10,440/6,560	9,200/5,135	9,000/6,740	7,470/6,440	8,780/6,300	9,000/6,570
	0.5	12,340/9,000	10,400/7,200	11,270/6,090	13,060/7,170	10,960/10,000	6,990/4,710	9,830/7,070
% elongation @break (MD/TD)	1.0	380/530	410/570	400/590	380/610	450/520	390/580	445/520
	0.5	267/400	240/390	290/540	290/500	290/350	276/310	280/520
Secant modulus (psi x 0.001), (MD/TD)	1.0	116/137	98/132	96/120	94/112	91/96	83/89	83/89
	0.5	114/136	96/113	97/119	64/113	90/99	98/102	88/95
Elmendorf Tear (g). (MD/TD)	1.0	17/180	17/260	16/383	18/320	136/520	50/184	53/440
	0.5	6/47	6/41	6/67	5/80	12/24	15/68	10/98
TD/MD tear balance	1.0	10.59	15.29	23.94	17.78	3.82	3.68	8.3
	0.5	7.83	6.83	11.17	16	2.0	4.53	9.8
Puncture Energy (in-lb/mil)	1.0	9.94	10.71	11.03	11.13	12.44	13.02	47.1
	0.5	12.93	12.33	10.63	12.33	14.72	NA	12.48

CLAIMS

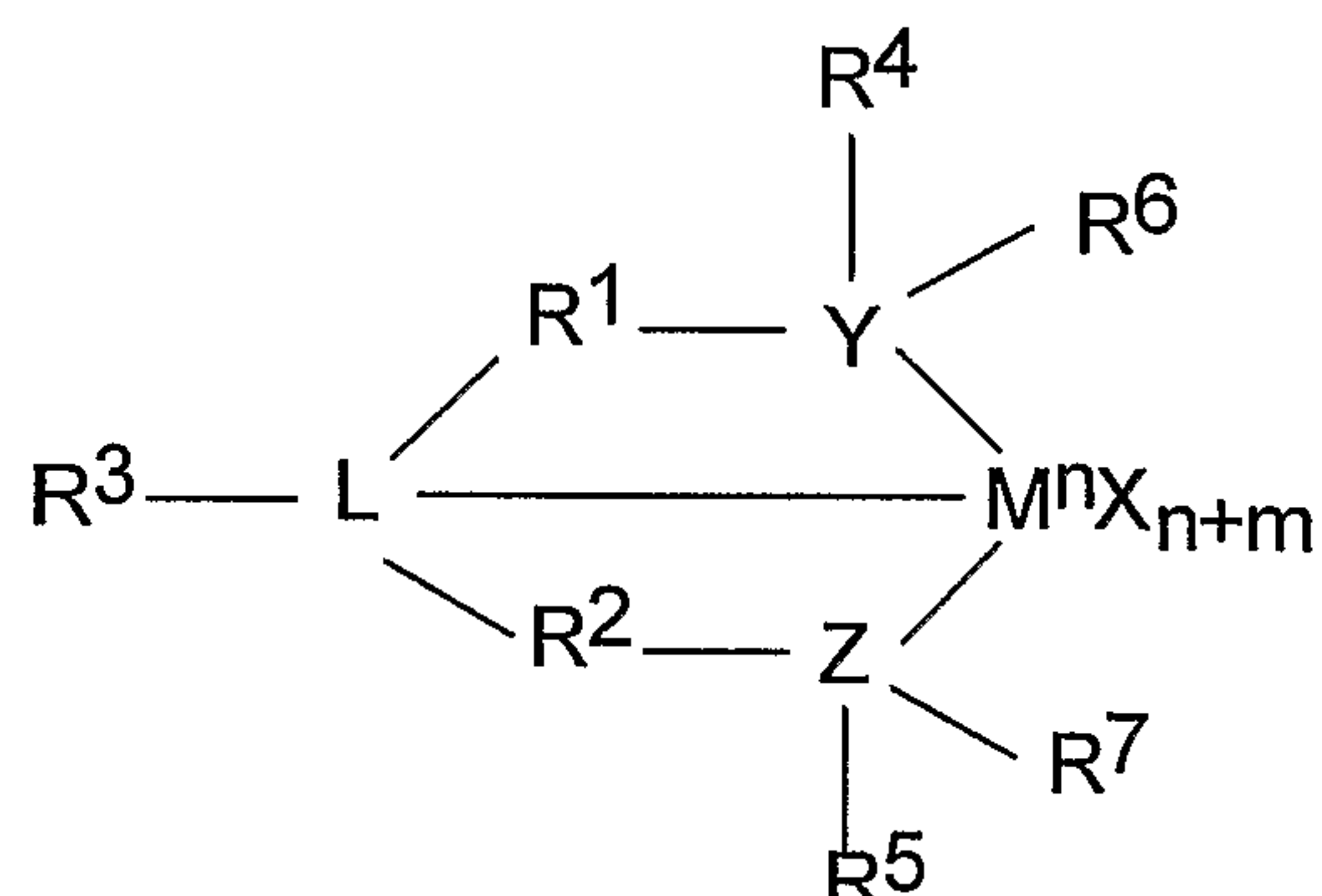
1. A high density multimodal polyethylene composition possessing a density of 0.935 g/cc or more, comprising a blend of a first polyethylene component and a second polyethylene component, wherein:

the first polyethylene component includes a bimodal polyethylene; and

the second polyethylene component is a unimodal polyethylene possessing a PDI value of less than 4.2;

characterized in that the high density multimodal polyethylene composition possesses a CLMS value of less than 10 wt% and a CHMS value of less than 24 wt%.
2. The composition of claims 1 or 2, in which the unimodal polyethylene comprises less than 20 wt% of the composition.
3. The composition of any of the preceding claims, wherein a 1.0 mil film made from the bimodal polyethylene high density multimodal polyethylene composition has an Elmendorf Tear ratio (TD/MD) of less than 8.
4. The composition of any of the preceding claims, wherein a 1.0 mil film made from the bimodal polyethylene high density multimodal polyethylene composition has an MD Elmendorf Tear of 100 grams or more.
5. The composition of any of the preceding claims, in which the PDI of the high density multimodal polyethylene composition is from 30 to 70.
6. The composition of any of the preceding claims, wherein the first polyethylene component includes a bimodal polyethylene that includes a high molecular weight component and a low molecular weight component, the bimodal polyethylene being made from a polymerization conducted in the presence of a dual catalyst system that comprises an activator and a metallocene.

7. The composition of Claim 6, wherein the catalyst system also comprises a fumed particulate filler and a catalyst compound represented by the formula:



wherein M is a Group 4, 5 or 6 metal;

each X is independently an anionic leaving group;

n is the oxidation state of M;

m is the formal charge of the ligand comprising Y, Z and L;

Y is a Group 15 atom;

Z is a Group 15 atom;

L is a Group 15 atom;

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, or a heteroatom containing group wherein the heteroatom is silicon, germanium, tin, lead, or phosphorus; optionally, R¹ and R² are interconnected to each other;

R³ is absent, a hydrogen, a group 14 atom containing group, a halogen, or a heteroatom containing group;

R⁴ and R⁵ are independently an alkyl group, an aryl group, a substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, or a multiple ring system; and

R⁶ and R⁷ are independently absent, a hydrogen, an alkyl group, a halogen, a heteroatom, a hydrocarbyl group, or a heteroatom containing group.

8. The composition of any of the preceding claims, wherein the unimodal polyethylene is produced from a polymerization conducted in the presence of a metallocene having two unbridged cyclopentadienyl rings.