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ETHYLENE-BASED POLYMER COMPOSITIONS**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of U.S. Provisional Application No. 61/222,371, filed July 1, 2009, and fully incorporated herein by reference.

BACKGROUND OF THE INVENTION

5 There have been many varieties of polyethylene polymers polymerized over the years, including those made using high pressure free radical chemistry (LDPE), more traditional linear low density polyethylene (LLDPE) typically made using Ziegler-Natta catalysis and metallocene or constrained geometry catalyzed polyethylene – some linear polyethylenes, but also some substantially linear
10 polyethylene containing a slight amount of long chain branching. While these polymers have varying positives and negatives – depending on application or end-use – more control over the polymer structure is still desired.

 We have now found that post-metallocene catalysts can efficiently polymerize
15 ethylene into polymers and polymer compositions having controlled comonomer distribution profiles, while also controlling unsaturation levels in the polymer.

BRIEF SUMMARY OF THE INVENTION

 In one embodiment, the invention is an ethylene-based polymer composition characterized by a Comonomer Distribution Constant greater than about 45, more
20 preferably greater than 50, most preferably greater than 95, and as high as 400, preferably as high as 200, wherein the composition has less than 120 total unsaturation unit/1,000,000C. Preferably, the ethylene-based polymer compositions comprise up to about 3 long chain branches/1000 carbons, more preferably from about 0.01 to about 3 long chain branches/1000 carbons. The ethylene-based polymer
25 composition can have a ZSVR of at least 2. The ethylene-based polymer compositions can be further characterized by comprising less than 20 vinylidene unsaturation unit/1,000,000C. The ethylene-based polymer compositions can have a bimodal molecular weight distribution (MWD) or a multi-modal MWD. The ethylene-based polymer compositions can have a comonomer distribution profile

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comprising a mono or bimodal distribution from 35oC to 120oC, excluding purge. The ethylene-based polymer compositions can comprise a single DSC melting peak. The ethylene-based polymer compositions can comprise a weight average molecular weight (Mw) from about 17,000 to about 220,000.

5 Fabricated articles comprising the novel polymer compositions are also contemplated, especially in the form of at least one film layer. Other embodiments include thermoplastic formulations comprising the novel polymer composition and at least one natural or synthetic polymer.

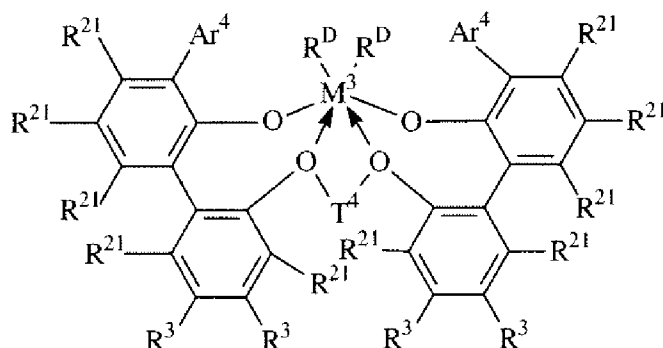
10 The ethylene-based polymer composition can be at least partially cross-linked (at least 5% (weight) gel).

In another embodiment, the invention is a process comprising:

(A) polymerizing ethylene in the presence of a first catalyst to form a semi-crystalline ethylene-based polymer in a first reactor or a first part of a multi-part reactor; and

(B) reacting the semi-crystalline ethylene-based polymer with additional ethylene in the presence of a second catalyst to form an ethylenic polymer in at least one other reactor or a later part of a multi-part reactor, wherein the catalyst of (A) and

20 (B) can be the same or different and each is a metal complex of a polyvalent aryloxyether corresponding to the formula:



where M³ is Ti, Hf or Zr, preferably Zr;

Ar⁴ independently each occurrence is a substituted C₉₋₂₀ aryl group, wherein the

25 substituents, independently each occurrence, are selected from the group consisting of alkyl; cycloalkyl; and aryl groups; and halo-, trihydrocarbysilyl- and halohydrocarbyl- substituted

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derivatives thereof, with the proviso that at least one substituent lacks co-planarity with the aryl group to which it is attached;

5 T^4 independently each occurrence is a C_{2-20} alkylene, cycloalkylene or cycloalkenylene group, or an inertly substituted derivative thereof;

10 R^{21} independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or di(hydrocarbyl)amino group of up to 50 atoms not counting hydrogen;

15 R^3 independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen, or two R^3 groups on the same arylene ring together or an R^3 and an R^{21} group on the same or different arylene ring together form a divalent ligand group attached to the arylene group in two positions or join two different arylene rings together; and

20 R^D , independently each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl, diene, or poly(hydrocarbyl)silylene group, especially where the reaction of step (B) occurs by graft polymerization.

In yet another embodiment, the invention is a method of characterizing an ethylene based polymer for comonomer composition distribution (CDC) comprising the following steps:

25 (A) Obtain a weight fraction at each temperature (T) ($w_T(T)$) from 35.0°C to 119.0°C with a temperature step of 0.200°C from CEF according to Equation 2,

$$\int_{35}^{119.0} w_T(T) dT = 1 \dots \dots \text{Equation 2}$$

(B) Calculate the mean temperature (T_{mean}) at cumulative weight fraction of 0.500 (Equation 3),

$$\int_{35}^{T_{mean}} w_T(T) dT = 0.5 \dots \dots \text{Equation 3}$$

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(C) Calculate the corresponding median comonomer content in mole % (C_{median}) at the median temperature (T_{median}) by using comonomer content calibration curve (Equation 4),

$$\ln(1 - \text{comonomercontent}) = -\frac{207.26}{273.12 + T} + 0.5533 \dots \text{Equation 4}$$

$$R^2 = 0.997$$

5 (D) Construct a comonomer content calibration curve by using a series of reference materials with known amount of comonomer content, eleven reference materials with narrow comonomer distribution (mono modal comonomer distribution in CEF from 35.0 to 119.0°C) with weight average Mw of 35,000 to 115,000 (by conventional GPC) at a comonomer content ranging from 0.0 mole% to 7.0mole% are
10 analyzed with CEF at the same experimental conditions specified in CEF experimental sections.

(E) Calculate comonomer content calibration by using the peak temperature (T_p) of each reference material and its comonomer content, the calibration is: R^2 is the correlation constant,

15 (F) Calculate Comonomer Distribution Index from the total weight fraction with a comonomer content ranging from $0.5 * C_{median}$ to $1.5 * C_{median}$, if T_{median} is higher than 98.0°C, Comonomer Distribution Index is defined as 0.95,

(G) Obtain Maximum peak height from CEF comonomer distribution profile by searching each data point for the highest peak from 35.0°C to 119.0°C (if the two
20 peaks are identical then the lower temperature peak is selected), half width is defined as the temperature difference between the front temperature and the rear temperature at the half of the maximum peak height, the front temperature at the half of the maximum peak is searched forward from 35.0°C, while the rear temperature at the half of the maximum peak is searched backward from 119.0°C, in the case of a well
25 defined bimodal distribution where the difference in the peak temperatures being equal to or larger than the sum of half width of each peak, the half- width of the polymer is calculated as the arithmetic average of the half width of each peak.

(H) Calculate the standard deviation of temperature ($Stdev$) according Equation 5:

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$$Stdev = \sqrt{\frac{119.0}{\sum_{35.0} (T - T_p)^2 * w_T(T)}} \dots \dots \text{Equation 5}$$

DETAILED DESCRIPTION OF THE INVENTION

In some processes, processing aids, such as plasticizers, can also be included in the ethylenic polymer product. These aids include, but are not limited to, the phthalates, such as dioctyl phthalate and diisobutyl phthalate, natural oils such as lanolin, and paraffin, naphthenic and aromatic oils obtained from petroleum refining, and liquid resins from rosin or petroleum feedstocks. Exemplary classes of oils useful as processing aids include white mineral oil such as KAYDOL oil (Chemtura Corp.; Middlebury, Conn.) and SHELLFLEX 371 naphthenic oil (Shell Lubricants; Houston, Tex.). Another suitable oil is TUFFLO oil (Lyondell Lubricants; Houston, Tex).

In some processes, ethylenic polymers are treated with one or more stabilizers, for example, antioxidants, such as IRGANOX 1010 and IRGAFOS 168 (Ciba Specialty Chemicals; Glattbrugg, Switzerland). In general, polymers are treated with one or more stabilizers before an extrusion or other melt processes. In other embodiment processes, other polymeric additives include, but are not limited to, ultraviolet light absorbers, antistatic agents, pigments, dyes, nucleating agents, fillers, slip agents, fire retardants, plasticizers, processing aids, lubricants, stabilizers, smoke inhibitors, viscosity control agents and anti-blocking agents. The ethylenic polymer composition may, for example, comprise less than 10 percent by the combined weight of one or more additives, based on the weight of the embodiment ethylenic polymer. A particular benefit of the claimed polymers is the absence of catalyst kill agents, other than water, thus eliminating the need for calcium stearate.

The ethylenic polymer produced may further be compounded. In some ethylenic polymer compositions, one or more antioxidants may further be compounded into the polymer and the compounded polymer pelletized. The compounded ethylenic polymer may contain any amount of one or more antioxidants. For example, the compounded ethylenic polymer may comprise from about 200 to about 600 parts of one or more phenolic antioxidants per one million parts of the

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polymer. In addition, the compounded ethylenic polymer may comprise from about 800 to about 1200 parts of a phosphite-based antioxidant per one million parts of polymer. The compounded disclosed ethylenic polymer may further comprise from about 300 to about 1250 parts of calcium stearate per one million parts of polymer.

5

Uses

The ethylenic polymer may be employed in a variety of conventional thermoplastic fabrication processes to produce useful articles, including objects comprising at least one film layer, such as a monolayer film, or at least one layer in a multilayer film prepared by cast, blown, calendered, or extrusion coating processes; 10 molded articles, such as blow molded, injection molded, or rotomolded articles; extrusions; fibers; and woven or non-woven fabrics. Thermoplastic compositions comprising the ethylenic polymer include blends with other natural or synthetic materials, polymers, additives, reinforcing agents, ignition resistant additives, 15 antioxidants, stabilizers, colorants, extenders, crosslinkers, blowing agents, and plasticizers.

The ethylenic polymer may be used in producing fibers for other applications. Fibers that may be prepared from the ethylenic polymer or blends thereof include 20 staple fibers, tow, multicomponent, sheath/core, twisted, and monofilament. Suitable fiber forming processes include spunbonded and melt blown techniques, as disclosed in U.S. Patent Nos. 4,340,563 (Appel, et al.), 4,663,220 (Wisneski, et al.), 4,668,566 (Nohr, et al.), and 4,322,027 (Reba), gel spun fibers as disclosed in U.S. Patent No. 4,413,110 (Kavesh, et al.), woven and nonwoven fabrics, as disclosed in U.S. Patent 25 No. 3,485,706 (May), or structures made from such fibers, including blends with other fibers, such as polyester, nylon or cotton, thermoformed articles, extruded shapes, including profile extrusions and co-extrusions, calendared articles, and drawn, twisted, or crimped yarns or fibers.

30 Additives and adjuvants may be added to the ethylenic polymer post-formation. Suitable additives include fillers, such as organic or inorganic particles, including clays, talc, titanium dioxide, zeolites, powdered metals, organic or inorganic fibers, including carbon fibers, silicon nitride fibers, steel wire or mesh, and nylon or polyester cording, nano-sized particles, clays, and so forth; tackifiers, oil extenders,

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including paraffinic or naphthelenic oils; and other natural and synthetic polymers, including other polymers that are or can be made according to the embodiment methods.

5 Blends and mixtures of the ethylenic polymer with other polyolefins may be performed. Suitable polymers for blending with the embodiment ethylenic polymer include thermoplastic and non-thermoplastic polymers including natural and synthetic polymers. Exemplary polymers for blending include polypropylene, (both impact
10 modifying polypropylene, isotactic polypropylene, atactic polypropylene, and random ethylene/propylene copolymers), various types of polyethylene, including high pressure, free-radical LDPE, Ziegler-Natta LLDPE, metallocene PE, including multiple reactor PE ("in reactor" blends of Ziegler-Natta PE and metallocene PE, such as products disclosed in U.S. Patent Nos. 6,545,088 (Kolthammer, et al.); 6,538,070 (Cardwell, et al.); 6,566,446 (Parikh, et al.); 5,844,045 (Kolthammer, et al.);
15 5,869,575 (Kolthammer, et al.); and 6,448,341 (Kolthammer, et al.)), ethylene-vinyl acetate (EVA), ethylene/vinyl alcohol copolymers, polystyrene, impact modified polystyrene, ABS, styrene/butadiene block copolymers and hydrogenated derivatives thereof (SBS and SEBS), and thermoplastic polyurethanes. Homogeneous polymers such as olefin plastomers and elastomers, ethylene and propylene-based copolymers
20 (for example, polymers available under the trade designation VERSIFY™ Plastomers & Elastomers (The Dow Chemical Company), SURPASS™ (Nova Chemicals), and VISTAMAXX™ (ExxonMobil Chemical Co.)) can also be useful as components in blends comprising the ethylenic polymer.

25 The ethylenic polymer maybe employed as a sealant resins. Surprisingly, certain SCBD, as shown by CDC, in combination with certain MWD, and a certain level of long chain branching (LCB) has shown to improve hot tack and heat seal performance, including increased hot-tack & heat-seal strength, lower heat seal and hot tack initiation temperatures, and a broadening of the hot tack window. The
30 ethylenic polymer maybe employed as a pipe and tubing resin through an optimization of the SCBD and MWD, with low unsaturation levels for improved ESCR (environmental stress crack resistance) and higher PENT (Pennsylvania Edge-Notch Tensile Test). The ethylenic polymer maybe employed in applications where UV stability, weatherability are desired through an optimization of the SCBD and

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MWD, in combination with low unsaturation levels, and low levels of low molecular weight, high comonomer incorporated oligomers. The ethylenic polymer maybe employed in applications where low levels of plate-out, blooming, die build-up, smoke formation, extractables, taste, and odor are desired through an optimization of the SCBD and MWD with low levels of low molecular weight, high comonomer incorporated oligomers. The ethylenic polymer maybe employed in stretch film applications. Surprisingly, certain SCBD, in combination with certain MWD, and a certain level of long chain branching (LCB) shows improved stretchability and dynamic puncture resistance.

Definitions

The term "composition," as used, includes a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

The terms "blend" or "polymer blend," as used, mean an intimate physical mixture (that is, without reaction) of two or more polymers. A blend may or may not be miscible (not phase separated at molecular level). A blend may or may not be phase separated. A blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and other methods known in the art. The blend may be effected by physically mixing the two or more polymers on the macro level (for example, melt blending resins or compounding) or the micro level (for example, simultaneous forming within the same reactor).

The term "linear" refers to polymers where the polymer backbone of the polymer lacks measurable or demonstrable long chain branches, for example, the polymer can be substituted with an average of less than 0.01 long branch per 1000 carbons.

The term "polymer" refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term "homopolymer," usually employed to refer to polymers prepared from only one type of monomer, and the term "interpolymer" as

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defined. The terms "ethylene/ α -olefin polymer" is indicative of interpolymers as described.

The term "interpolymer" refers to polymers prepared by the polymerization of
5 at least two different types of monomers. The generic term interpolymer includes copolymers, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different types of monomers. The term "ethylene-based polymer" refers to a polymer that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of
10 polymerizable monomers) and, optionally, may contain at least one comonomer.

The term "ethylene/ α -olefin interpolymer" refers to an interpolymer that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of polymerizable monomers) and at least one α -olefin.
15

The term "ethylenic polymer" refers to a polymer resulting from the intermolecular bonding of a crystalline ethylene-based polymer and at least one highly long chain branched ethylene-based polymer.

20 **Resin Production**

All raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent trademarked Isopar E and commercially available from Exxon Mobil Corporation) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied in
25 pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized via mechanical compressor to above reaction pressure at 750 psig. The solvent and comonomer (1-octene) feed is pressurized via mechanical positive displacement pump to above reaction pressure at 750 psig. The individual catalyst components are manually batch diluted to specified
30 component concentrations with purified solvent (Isopar E) and pressured to above reaction pressure at 750 psig. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

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The continuous solution polymerization reactors consist of two liquid full, non-adiabatic, isothermal, circulating, and independently controlled loops operating in a series configuration. Each reactor has independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds. The combined
5 solvent, monomer, comonomer and hydrogen feed to each reactor is independently temperature controlled to anywhere between 5°C to 50°C and typically 40°C by passing the feed stream through a heat exchanger. The fresh comonomer feed to the polymerization reactors can be manually aligned to add comonomer to one of three choices: the first reactor, the second reactor, or the common solvent and then split
10 between both reactors proportionate to the solvent feed split. The total fresh feed to each polymerization reactor is injected into the reactor at two locations per reactor roughly with equal reactor volumes between each injection location. The fresh feed is controlled typically with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor through specially
15 designed injection stingers and are each separately injected into the same relative location in the reactor with no contact time prior to the reactor. The primary catalyst component feed is computer controlled to maintain the reactor monomer concentration at a specified target. The two cocatalyst components are fed based on calculated specified molar ratios to the primary catalyst component. Immediately
20 following each fresh injection location (either feed or catalyst), the feed streams are mixed with the circulating polymerization reactor contents with Kenics static mixing elements. The contents of each reactor are continuously circulated through heat exchangers responsible for removing much of the heat of reaction and with the temperature of the coolant side responsible for maintaining isothermal reaction
25 environment at the specified temperature. Circulation around each reactor loop is provided by a screw pump. The effluent from the first polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits the first reactor loop and passes through a control valve (responsible for maintaining the pressure of the first reactor at a specified target) and
30 is injected into the second polymerization reactor of similar design. As the stream exits the reactor it is contacted with water to stop the reaction. In addition, various additives such as anti-oxidants, can be added at this point. The stream then goes through another set of Kenics static mixing elements to evenly disperse the catalyst kill and additives.

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Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passes through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower boiling reaction components. The stream then enters a two stage separation and devolatilization system where the polymer is removed from the solvent, hydrogen, and unreacted monomer and comonomer. The recycled stream is purified before entering the reactor again. The separated and devolatilized polymer melt is pumped through a die specially designed for underwater pelletization, cut into uniform solid pellets, dried, and transferred into a hopper. After validation of initial polymer properties the solid polymer pellets are manually dumped into a box for storage. Each box typically holds ~1200 pounds of polymer pellets.

The non-polymer portions removed in the devolatilization step pass through various pieces of equipment which separate most of the ethylene which is removed from the system to a vent destruction unit (it is recycled in manufacturing units). Most of the solvent is recycled back to the reactor after passing through purification beds. This solvent can still have unreacted co-monomer in it that is fortified with fresh co-monomer prior to re-entry to the reactor. This fortification of the co-monomer is an essential part of the product density control method. This recycle solvent can still have some hydrogen which is then fortified with fresh hydrogen to achieve the polymer molecular weight target. A very small amount of solvent leaves the system as a co-product due to solvent carrier in the catalyst streams and a small amount of solvent that is part of commercial grade co-monomers.

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	<i>Run #</i>	<i>Ex. 3</i> <i>08C16R04</i>	<i>Ex. 1</i> <i>08C16R05</i>	<i>Ex. 2</i> <i>09C05R07V1</i>
Primary Reactor Feed Temperature	°C	20	20	20
Primary Reactor Total Solvent Flow	lbs/h	1159	1161	1160
Primary Reactor Total Ethylene Flow	lbs/h	220	178	199
Primary Reactor Total Comonomer Flow	lbs/h	92	76	15
Primary Reactor Feed Solvent/Ethylene Ratio	Ratio	5.5	6.9	6.9
Primary Reactor Fresh Hydrogen Flow	sccm	6485	3383	701
Secondary Reactor Feed Temperature	°C	20	21	32
Secondary Reactor Total Solvent Flow	lbs/h	400	510	340
Secondary Reactor Total Ethylene Flow	lbs/h	153	196	127
Secondary Reactor Total Comonomer Flow	lbs/h	16.1	13.5	1.8
Secondary Reactor Feed Solvent/Ethylene Ratio	Ratio	2.7	2.7	2.8
Secondary Reactor Fresh Hydrogen Flow	sccm	2047	4990	21857
Primary Reactor Control Temperature	°C	155	140	180
Primary Reactor Pressure	psig	725	725	725
Primary Reactor Ethylene Conversion	%	81	92	91
Primary Reactor Percent Solids	%	16	16	13
E-214B Heat Transfer Coefficient	BTU/hr ft ³ °F	7.6	6.7	9.1
Primary Reactor Polymer Residence Time	hrs	0.25	0.27	0.29
Secondary Reactor Control Temperature	°C	190	190	190
Secondary Reactor Pressure	psig	729	731	730
Secondary Reactor Ethylene Conversion	%	87	87	85
Secondary Reactor Percent Solids	%	22	21	17
E-216B Heat Transfer Coefficient	BTU/hr ft ³ °F	80	51	44
Secondary Reactor Polymer Residence Time	hrs	0.10	0.10	0.12
Primary Reactor Split	%	53	50	56
Primary Reactor Production Rate	lbs/h	226	212	160
Secondary Reactor Production Rate	lbs/h	201	215	127
Total production rate from MB	lbs/h	427	426	287
Primary Reactor Catalyst Efficiency	MM Lb	10.9	8.6	2.3
Secondary Reactor Catalyst Efficiency	MM Lb	1.4	1.6	1.1

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	<i>Time Run #</i>	<i>Ex. 3 08C16R04</i>	<i>Ex. 1 08C16R05</i>	<i>Ex. 2 09C05R07V1</i>
3. CATALYST				
Primary Reactor Catalyst Type	-	DOC-6114	DOC-6114	DOC-6114
Primary Reactor Catalyst Flow	lbs/h	1.52	1.81	1.962124
Primary Reactor Catalyst Concentration	ppm	13.67	13.67	34.95987
Primary Reactor Catalyst Efficiency	MM Lb	10.87	8.56	2.309096
Primary Reactor Catalyst-1 Type	-	DOC-6114	DOC-6114	DOC-6114
Primary Reactor Catalyst-1 Flow	lbs/h	1.52	1.81	1.96
Primary Reactor Catalyst-1 Concentration	ppm	13.67	13.67	34.96
Primary Reactor Catalyst-1 Mole Weight	mw	90.86	90.86	90.86
Primary Reactor Co-Catalyst-1 Molar Ratio	Ratio	1.77	1.48	1.42
Primary Reactor Co-Catalyst-1 Type	-	MMAO	MMAO	MMAO
Primary Reactor Co-Catalyst-1 Flow	lbs/h	0.81	0.81	1.19
Primary Reactor Co-Catalyst-1 Concentration	ppm	596	596	1094
Primary Reactor Co-Catalyst-2 Molar Ratio	Ratio	7.11	6.91	6.97
Primary Reactor Co-Catalyst-2 Type	-	RIBS-2	RIBS-2	RIBS-2
Primary Reactor Co-Catalyst-2 Flow	lbs/h	0.44	0.52	0.72
Primary Reactor Co-Catalyst-2 Concentration	ppm	99.6	99.6	199
Secondary Reactor Catalyst Type	See Note	DOC-6114	DOC-6114	DOC-6114
Secondary Reactor Catalyst Flow	lbs/h	3.52	2.30	1.54
Secondary Reactor Catalyst Concentration	ppm	40	60	76
Secondary Reactor Catalyst Efficiency	MM Lb	1.43	1.56	1.08
Secondary Reactor Co-Catalyst-1 Molar Ratio	Ratio	1.48	1.50	1.21
Secondary Reactor Co-Catalyst-1 Type	See Note	MMAO	MMAO	MMAO
Secondary Reactor Co-Catalyst-1 Flow	lbs/h	4.62	4.59	1.68
Secondary Reactor Co-Catalyst-1 Concentration	ppm	596	596	1094
Secondary Reactor Co-Catalyst-2 Molar Ratio	Ratio	6.99	7.02	6.96
Secondary Reactor Co-Catalyst-2 Type	See Note	RIBS-2	RIBS-2	RIBS-2
Secondary Reactor Co-Catalyst-2 Flow	lbs/h	2.93	2.88	1.22
Secondary Reactor Co-Catalyst-2 Concentration	ppm	100	100	199

CAS name for RIBS-2: Amines, bis(hydrogenated tallow alkyl)methyl,
tetrakis(pentafluorophenyl)borate(1-)

CAS name for DOC-6114: Zirconium, [2,2"-[1,3-propanediylbis(oxy-κO)]bis[3",5,5"-tris(1,1-dimethylethyl)-5'-methyl[1,1':3',1"-terphenyl]-2'-olato-κO]]dimethyl-, (OC-6-33)-
MMAO = modified methyl aluminoxane

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TEST METHODS**Density**

Samples that are measured for density are prepared according to ASTM D 1928. Measurements are made within one hour of sample pressing using ASTM
5 D792, Method B.

Melt Index

Melt index, or I_2 , is measured in accordance with ASTM D 1238, Condition 190 °C/2.16 kg, and is reported in grams eluted per 10 minutes. I_{10} is measured in
10 accordance with ASTM D 1238, Condition 190 °C/10 kg, and is reported in grams eluted per 10 minutes.

DSC Crystallinity

Differential Scanning Calorimetry (DSC) can be used to measure the melting
15 and crystallization behavior of a polymer over a wide range of temperature. For example, the TA Instruments Q1000 DSC, equipped with an RCS (refrigerated cooling system) and an autosampler is used to perform this analysis. During testing, a nitrogen purge gas flow of 50 ml/min is used. Each sample is melt pressed into a thin film at about 175 °C; the melted sample is then air-cooled to room temperature (~25
20 °C). A 3-10 mg, 6 mm diameter specimen is extracted from the cooled polymer, weighed, placed in a light aluminum pan (ca 50 mg), and crimped shut. Analysis is then performed to determine its thermal properties.

The thermal behavior of the sample is determined by ramping the sample
25 temperature up and down to create a heat flow versus temperature profile. First, the sample is rapidly heated to 180 °C and held isothermal for 3 minutes in order to remove its thermal history. Next, the sample is cooled to -40 °C at a 10 °C/minute cooling rate and held isothermal at -40 °C for 3 minutes. The sample is then heated to 150 °C (this is the “second heat” ramp) at a 10 °C/minute heating rate. The cooling
30 and second heating curves are recorded. The cool curve is analyzed by setting baseline endpoints from the beginning of crystallization to -20 °C. The heat curve is analyzed by setting baseline endpoints from -20 °C to the end of melt. The values determined are peak melting temperature (T_m), peak crystallization temperature (T_c),

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heat of fusion (H_f) (in Joules per gram), and the calculated % crystallinity for polyethylene samples using Equation 2:

$$\% \text{ Crystallinity} = ((H_f)/(292 \text{ J/g})) \times 100 \quad (\text{Eq. 2}).$$

- 5 The heat of fusion (H_f) and the peak melting temperature are reported from the second heat curve. Peak crystallization temperature is determined from the cooling curve.

Dynamic Mechanical Spectroscopy (DMS) Frequency Sweep

- 10 Melt rheology, constant temperature frequency sweeps, were performed using a TA Instruments ARES rheometer equipped with 25 mm parallel plates under a nitrogen purge. Frequency sweeps were performed at 190 °C for all samples at a gap of 2.0 mm and at a constant strain of 10%. The frequency interval was from 0.1 to 100 radians/second. The stress response was analyzed in terms of amplitude and phase, from which the storage
15 modulus (G'), loss modulus (G''), and dynamic melt viscosity (η^*) were calculated.

Gel Permeation Chromatography (GPC)

- The GPC system consists of a Waters (Milford, MA) 150C high temperature chromatograph (other suitable high temperatures GPC instruments include Polymer
20 Laboratories (Shropshire, UK) Model 210 and Model 220) equipped with an on-board differential refractometer (RI). Additional detectors can include an IR4 infra-red detector from Polymer ChAR (Valencia, Spain), Precision Detectors (Amherst, MA) 2-angle laser light scattering detector Model 2040, and a Viscotek (Houston, TX) 150R 4-capillary solution viscometer. A GPC with the last two independent detectors
25 and at least one of the first detectors is sometimes referred to as "3D-GPC", while the term "GPC" alone generally refers to conventional GPC. Depending on the sample, either the 15-degree angle or the 90-degree angle of the light scattering detector is used for calculation purposes. Data collection is performed using Viscotek TriSEC software, Version 3, and a 4-channel Viscotek Data Manager DM400. The system is
30 also equipped with an on-line solvent degassing device from Polymer Laboratories (Shropshire, UK). Suitable high temperature GPC columns can be used such as four 30 cm long Shodex HT803 13 micron columns or four 30 cm Polymer Labs columns of 20-micron mixed-pore-size packing (MixA LS, Polymer Labs). The sample carousel compartment is operated at 140 °C and the column compartment is operated

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at 150 °C. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The chromatographic solvent and the sample preparation solvent contain 200 ppm of butylated hydroxytoluene (BHT). Both solvents are sparged with nitrogen. The polyethylene samples are gently stirred at 160 °C for four
5 hours. The injection volume is 200 microliters. The flow rate through the GPC is set at 1 ml/minute.

The GPC column set is calibrated before running the Examples by running twenty-one narrow molecular weight distribution polystyrene standards. The
10 molecular weight (MW) of the standards ranges from 580 to 8,400,000 grams per mole, and the standards are contained in 6 “cocktail” mixtures. Each standard mixture has at least a decade of separation between individual molecular weights. The standard mixtures are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 g in 50 mL of solvent for molecular
15 weights equal to or greater than 1,000,000 grams per mole and 0.05 g in 50 ml of solvent for molecular weights less than 1,000,000 grams per mole. The polystyrene standards were dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular
20 weights are converted to polyethylene M_w using the Mark-Houwink K and a (sometimes referred to as α) values mentioned later for polystyrene and polyethylene. See the Examples section for a demonstration of this procedure.

With 3D-GPC absolute weight average molecular weight (“ $M_{w, Abs}$ ”) and
25 intrinsic viscosity are also obtained independently from suitable narrow polyethylene standards using the same conditions mentioned previously. These narrow linear polyethylene standards may be obtained from Polymer Laboratories (Shropshire, UK; Part No.’s PL2650-0101 and PL2650-0102).

30 The systematic approach for the determination of multi-detector offsets is performed in a manner consistent with that published by Balke, Mourey, et al. (Mourey and Balke, *Chromatography Polym.*, Chapter 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, *Chromatography Polym.*, Chapter 13, (1992)), optimizing triple detector log (M_w and intrinsic viscosity) results from Dow 1683

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broad polystyrene (American Polymer Standards Corp.; Mentor, OH) or its equivalent to the narrow standard column calibration results from the narrow polystyrene standards calibration curve. The molecular weight data, accounting for detector volume off-set determination, are obtained in a manner consistent with that published by Zimm (Zimm, B.H., *J. Chem. Phys.*, 16, 1099 (1948)) and Kratochvil (Kratochvil, P., *Classical Light Scattering from Polymer Solutions*, Elsevier, Oxford, NY (1987)). The overall injected concentration used in the determination of the molecular weight is obtained from the mass detector area and the mass detector constant derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards. The calculated molecular weights are obtained using a light scattering constant derived from one or more of the polyethylene standards mentioned and a refractive index concentration coefficient, dn/dc , of 0.104. Generally, the mass detector response and the light scattering constant should be determined from a linear standard with a molecular weight in excess of about 50,000 daltons. The viscometer calibration can be accomplished using the methods described by the manufacturer or alternatively by using the published values of suitable linear standards such as Standard Reference Materials (SRM) 1475a, 1482a, 1483, or 1484a. The chromatographic concentrations are assumed low enough to eliminate addressing 2nd viral coefficient effects (concentration effects on molecular weight).

20

g' by 3D-GPC

The index (g') for the sample polymer is determined by first calibrating the light scattering, viscosity, and concentration detectors described in the Gel Permeation Chromatography method *supra* with SRM 1475a homopolymer polyethylene (or an equivalent reference). The light scattering and viscometer detector offsets are determined relative to the concentration detector as described in the calibration. Baselines are subtracted from the light scattering, viscometer, and concentration chromatograms and integration windows are then set making certain to integrate all of the low molecular weight retention volume range in the light scattering and viscometer chromatograms that indicate the presence of detectable polymer from the refractive index chromatogram. A linear homopolymer polyethylene is used to establish a Mark-Houwink (MH) linear reference line by injecting a broad molecular weight polyethylene reference such as SRM1475a standard, calculating the data file, and recording the intrinsic viscosity (IV) and molecular weight (M_w), each derived

30

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from the light scattering and viscosity detectors respectively and the concentration as determined from the RI detector mass constant for each chromatographic slice. For the analysis of samples the procedure for each chromatographic slice is repeated to obtain a sample Mark-Houwink line. Note that for some samples the lower molecular weights, the intrinsic viscosity and the molecular weight data may need to be extrapolated such that the measured molecular weight and intrinsic viscosity asymptotically approach a linear homopolymer GPC calibration curve. To this end, many highly-branched ethylene-based polymer samples require that the linear reference line be shifted slightly to account for the contribution of short chain branching before proceeding with the long chain branching index (g') calculation.

A g' -prime (g'_i) is calculated for each branched sample chromatographic slice (i) and measuring molecular weight (M_i) according to Equation 5:

$$g'_i = (IV_{\text{Sample},i} / IV_{\text{linear reference},j}) \quad (\text{Eq. 5}),$$

where the calculation utilizes the $IV_{\text{linear reference},j}$ at equivalent molecular weight, M_j , in the linear reference sample. In other words, the sample IV slice (i) and reference IV slice (j) have the same molecular weight ($M_i = M_j$). For simplicity, the $IV_{\text{linear reference},j}$ slices are calculated from a fifth-order polynomial fit of the reference Mark-Houwink Plot. The IV ratio, or g'_i , is only obtained at molecular weights greater than 3,500 because of signal-to-noise limitations in the light scattering data. The number of branches along the sample polymer (B_n) at each data slice (i) can be determined by using Equation 6, assuming a viscosity shielding epsilon factor of 0.75:

$$\left[\frac{IV_{\text{Sample},i}}{IV_{\text{linear_reference},j}} \right]_{M_i=M_j}^{1.33} = \left[\left(1 + \frac{B_{n,i}}{7} \right)^{1/2} + \frac{4}{9} \frac{B_{n,i}}{\pi} \right]^{-1/2} \quad (\text{Eq. 6}).$$

Finally, the average LCBf quantity per 1000 carbons in the polymer across all of the slices (i) can be determined using Equation 7:

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$$LCBf = \frac{\sum_i \left(\frac{B_{n,i}}{M_i / 14000} c_i \right)}{\sum c_i} \quad (\text{Eq. 7}).$$

gpcBR Branching Index by 3D-GPC

In the 3D-GPC configuration the polyethylene and polystyrene standards can be used to measure the Mark-Houwink constants, K and α , independently for each of the two polymer types, polystyrene and polyethylene. These can be used to refine the Williams and Ward polyethylene equivalent molecular weights in application of the following methods.

The gpcBR branching index is determined by first calibrating the light scattering, viscosity, and concentration detectors as described previously. Baselines are then subtracted from the light scattering, viscometer, and concentration chromatograms. Integration windows are then set to ensure integration of all of the low molecular weight retention volume range in the light scattering and viscometer chromatograms that indicate the presence of detectable polymer from the refractive index chromatogram. Linear polyethylene standards are then used to establish polyethylene and polystyrene Mark-Houwink constants as described previously. Upon obtaining the constants, the two values are used to construct two linear reference conventional calibrations ("cc") for polyethylene molecular weight and polyethylene intrinsic viscosity as a function of elution volume, as shown in Equations 8 and 9:

$$M_{PE} = \left(\frac{K_{PS}}{K_{PE}} \right)^{1/\alpha_{PE}+1} \cdot M_{PS}^{\alpha_{PS} \cdot 1/\alpha_{PE}+1} \quad (\text{Eq. 8}), \text{ and}$$

$$[\eta]_{PE} = K_{PS} \cdot M_{PS}^{\alpha+1} / M_{PE} \quad (\text{Eq. 9}).$$

The gpcBR branching index is a robust method for the characterization of long chain branching. See Yau, Wallace W., "Examples of Using 3D-GPC ~ TREF for Polyolefin Characterization", *Macromol. Symp.*, 2007, 257, 29-45. The index avoids

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- the slice-by-slice 3D-GPC calculations traditionally used in the determination of g' values and branching frequency calculations in favor of whole polymer detector areas and area dot products. From 3D-GPC data, one can obtain the sample bulk M_w by the light scattering (LS) detector using the peak area method. The method avoids the
- 5 slice-by-slice ratio of light scattering detector signal over the concentration detector signal as required in the g' determination.

$$M_w = \sum_i w_i M_i = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) M_i = \frac{\sum_i C_i M_i}{\sum_i C_i} = \frac{\sum_i LS_i}{\sum_i C_i} = \frac{LS \text{ Area}}{Conc. \text{ Area}} \quad (\text{Eq. 10}).$$

- 10 The area calculation in Equation 10 offers more precision because as an overall sample area it is much less sensitive to variation caused by detector noise and GPC settings on baseline and integration limits. More importantly, the peak area calculation is not affected by the detector volume offsets. Similarly, the high-precision sample intrinsic viscosity (IV) is obtained by the area method shown in
- 15 Equation 11:

$$IV = [\eta] = \sum_i w_i IV_i = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \frac{\sum_i C_i IV_i}{\sum_i C_i} = \frac{\sum_i DP_i}{\sum_i C_i} = \frac{DP \text{ Area}}{Conc. \text{ Area}} \quad (\text{Eq. 11}),$$

- 20 where DP_i stands for the differential pressure signal monitored directly from the online viscometer.

- To determine the gpcBR branching index, the light scattering elution area for the sample polymer is used to determine the molecular weight of the sample. The
- 25 viscosity detector elution area for the sample polymer is used to determine the intrinsic viscosity (IV or $[\eta]$) of the sample.

Initially, the molecular weight and intrinsic viscosity for a linear polyethylene standard sample, such as SRM1475a or an equivalent, are determined using the

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conventional calibrations for both molecular weight and intrinsic viscosity as a function of elution volume, per Equations 12 and 13:

$$M_{w,cc} = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) M_i = \sum_i w_i M_i \quad (\text{Eq. 12}), \text{ and}$$

5

$$[\eta]_{cc} = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \sum_i w_i IV_i \quad (\text{Eq. 13}).$$

Equation 14 is used to determine the gpcBR branching index:

$$10 \quad gpcBR = \left[\left(\frac{[\eta]_{cc}}{[\eta]} \right) \cdot \left(\frac{M_w}{M_{w,cc}} \right)^{\alpha_{pk}} - 1 \right] \quad (\text{Eq. 14}),$$

where $[\eta]$ is the measured intrinsic viscosity, $[\eta]_{cc}$ is the intrinsic viscosity from the conventional calibration, M_w is the measured weight average molecular weight, and $M_{w,cc}$ is the weight average molecular weight of the conventional calibration. The M_w by light scattering (LS) using Equation (10) is commonly referred to as the absolute M_w ; while the $M_{w,cc}$ from Equation (12) using the conventional GPC molecular weight calibration curve is often referred to as polymer chain M_w . All statistical values with the “cc” subscript are determined using their respective elution volumes, the corresponding conventional calibration as previously described, and the concentration (C_i) derived from the mass detector response. The non-subscripted values are measured values based on the mass detector, LALLS, and viscometer areas. The value of K_{PE} is adjusted iteratively until the linear reference sample has a gpcBR measured value of zero. For example, the final values for α and Log K for the determination of gpcBR in this particular case are 0.725 and -3.355, respectively, for polyethylene, and 0.722 and -3.993 for polystyrene, respectively.

Once the K and α values have been determined, the procedure is repeated using the branched samples. The branched samples are analyzed using the final

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Mark-Houwink constants as the best “cc” calibration values and applying Equations 10-14.

The interpretation of gpcBR is straight forward. For linear polymers, gpcBR
5 calculated from Equation 14 will be close to zero since the values measured by LS
and viscometry will be close to the conventional calibration standard. For branched
polymers, gpcBR will be higher than zero, especially with high levels of LCB,
because the measured polymer M_w will be higher than the calculated $M_{w,cc}$, and the
calculated IV_{cc} will be higher than the measured polymer IV. In fact, the gpcBR
10 value represents the fractional IV change due the molecular size contraction effect as
the result of polymer branching. A gpcBR value of 0.5 or 2.0 would mean a
molecular size contraction effect of IV at the level of 50% and 200%, respectively,
versus a linear polymer molecule of equivalent weight.

15 For these particular Examples, the advantage of using gpcBR in comparison to
the g' index and branching frequency calculations is due to the higher precision of
gpcBR. All of the parameters used in the gpcBR index determination are obtained
with good precision and are not detrimentally affected by the low 3D-GPC detector
response at high molecular weight from the concentration detector. Errors in detector
20 volume alignment also do not affect the precision of the gpcBR index determination.
In other particular cases, other methods for determining M_w moments may be
preferable to the aforementioned technique.

Unless otherwise stated, implicit from the context or conventional in the art,
25 all parts and percentages are based on weight.

All applications, publications, patents, test procedures, and other documents
cited, including priority documents, are fully incorporated by reference to the extent
such disclosure is not inconsistent with the disclosed compositions and methods and
30 for all jurisdictions in which such incorporation is permitted.

CEF Method

Comonomer distribution analysis is performed with Crystallization Elution
Fractionation (CEF) (PolymerChar in Spain) (B Monrabal et al, Macromol. Symp.

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257, 71-79 (2007)). Ortho-dichlorobenzene (ODCB) with 600ppm antioxidant butylated hydroxytoluene (BHT) is used as solvent. Sample preparation is done with autosampler at 160oC for 2 hours under shaking at 4 mg/ml (unless otherwise specified). The injection volume is 300 µl. The temperature profile of CEF is:
 5 crystallization at 3oC/min from 110 oC to 30 oC, the thermal equilibrium at 30 oC for 5 minutes, elution at 3oC/min from 30oC to 140 oC. The flow rate during crystallization is at 0.052 ml/min. The flow rate during elution is at 0.50 ml/min. The data is collected at one data point/second.

10 CEF column is packed by the Dow Chemical Company with glass beads at 125 um± 6% (MO-SCI Specialty Products) with 1/8 inch stainless tubing. Glass beads are acid washed by MO-SCI Specialty with the request from the Dow Chemical Company. Column volume is 2.06 ml. Column temperature calibration is performed by using a mixture of NIST Standard Reference Material Linear polyethylene 1475a
 15 (1.0mg/ml) and Eicosane (2mg/ml) in ODCB. Temperature is calibrated by adjusting elution heating rate so that NIST linear polyethylene 1475a has a peak temperature at 101.0oC, and Eicosane has a peak temperature of 30.0oC. The CEF column resolution is calculated with a mixture of NIST linear polyethylene 1475a (1.0mg/ml) and hexacontane (Fluka, purum, ≥97.0%, 1mg/ml). A baseline separation of hexacontane
 20 and NIST polyethylene 1475a is achieved. The area of hexacontane (from 35.0 to 67.0oC) to the area of NIST 1475a from 67.0 to 110.0oC is 50 to 50, the amount of soluble fraction below 35.0oC is <1.8 wt%.

The CEF column resolution is defined as:

$$25 \text{ Resolution} = \frac{\text{Peak temperature of NIST 1475a} - \text{Peak Temperature of Hexacontane}}{\text{Half - height Width of NIST 1475a} + \text{Half - height Width of Hexacontane}}$$

The column resolution is 6.0

CDC Method

30 Comonomer distribution constant (CDC) is calculated from comonomer distribution profile by CEF. CDC is defined as Comonomer Distribution Index divided by Comonomer Distribution Shape Factor multiplying by 100 (Equation 1)

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$$CDC = \frac{\text{Comonomer Distribution Index}}{\text{Comonomer Distribution Shape Factor}} = \frac{\text{Comonomer Distribution Index}}{\text{Half Width/Stddev}} * 100 \dots \text{Equation 1}$$

Comonomer distribution index stands for the total weight fraction of polymer chains with the comonomer content ranging from 0.5 of median comonomer content (C_{median}) and 1.5 of C_{median} from 35.0 to 119.0°C. Comonomer Distribution Shape Factor is defined as a ratio of the half width of comonomer distribution profile divided by the standard deviation of comonomer distribution profile from the peak temperature (T_p).

CDC is calculated according to the following steps:
Obtain weight fraction at each temperature (T) ($w_T(T)$) from 35.0°C to 119.0°C with a temperature step of 0.200°C from CEF according to Equation 2.

$$\int_{35}^{119.0} w_T(T) dT = 1 \dots \text{Equation 2}$$

Calculate the mean temperature (T_{mean}) at cumulative weight fraction of 0.500 (Equation 3)

$$\int_{35}^{T_{\text{mean}}} w_T(T) dT = 0.5 \dots \text{Equation 3}$$

Calculate the corresponding median comonomer content in mole % (C_{median}) at the median temperature (T_{median}) by using comonomer content calibration curve (Equation 4).

$$\ln(1 - \text{comonomer content}) = -\frac{207.26}{273.12 + T} + 0.5533 \dots \text{Equation 4}$$

$$R^2 = 0.997$$

(3i). Comonomer content calibration curve is constructed by using a series of reference materials with known amount of comonomer content. Eleven reference materials with narrow comonomer distribution (mono modal comonomer distribution

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in CEF from 35.0 to 119.0°C) with weight average Mw of 35,000 to 115,000 (by conventional GPC) at a comonomer content ranging from 0.0 mole% to 7.0mole% are analyzed with CEF at the same experimental conditions specified in CEF experimental sections.

- 5 (3ii). Comonomer content calibration is calculated by using the peak temperature (T_p) of each reference material and its comonomer content. The calibration is: R^2 is the correlation constant.

Comonomer Distribution Index is the total weight fraction with a comonomer content ranging from $0.5 * C_{median}$ to $1.5 * C_{median}$. If T_{median} is higher than 98.0°C,

- 10 Comonomer Distribution Index is defined as 0.95.

Maximum peak height is obtained from CEF comonomer distribution profile by searching each data point for the highest peak from 35.0°C to 119.0°C (if the two peaks are identical then the lower temperature peak is selected) Half width is defined as the temperature difference between the front temperature and the rear temperature

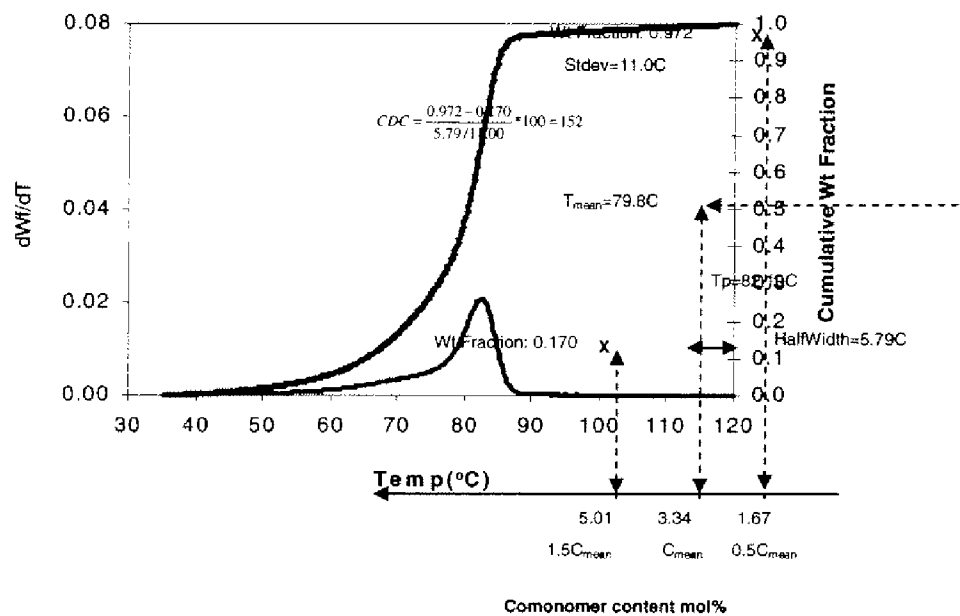
- 15 at the half of the maximum peak height. The front temperature at the half of the maximum peak is searched forward from 35.0°C, while the rear temperature at the half of the maximum peak is searched backward from 119.0°C. In the case of a well defined bimodal distribution where the difference in the peak temperatures being equal to or larger than 1.1 times of the sum of half width of each peak, the half- width
20 of the polymer is calculated as the arithmetic average of the half width of each peak.

The standard deviation of temperature ($Stdev$) is calculated according Equation 5:

$$Stdev = \sqrt{\sum_{35.0}^{119.0} (T - T_p)^2 * w_T(T)} \dots \dots \text{Equation 5}$$

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An example (Ex.3 08C16R04) of comonomer distribution profile is shown in Figure*.



5

Figure . Schematic drawings for obtaining peak temperature, half width and median temperature from CEF.

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Creep zero shear viscosity measurement method:

Zero-shear viscosities are obtained via creep tests that were conducted on an AR-G2 stress controlled rheometer (TA Instruments; New Castle, Del) using 25-mm-diameter parallel plates at 190°C. The rheometer oven is set to test temperature for at least 30 minutes prior to zeroing fixtures. At the testing temperature a compression molded sample disk is inserted between the plates and allowed to come to equilibrium for 5 minutes. The upper plate is then lowered down to 50 μm above the desired testing gap (1.5 mm). Any superfluous material is trimmed off and the upper plate is lowered to the desired gap. Measurements are done under nitrogen purging at a flow rate of 5 L/min. Default creep time is set for 2 hours.

A constant low shear stress of 20 Pa is applied for all of the samples to ensure that the steady state shear rate is low enough to be in the Newtonian region. The resulting steady state shear rates are in the range of 10^{-3} to 10^{-4} s $^{-1}$ for the samples in this study. Steady state is determined by taking a linear regression for all the data in the last 10% time window of the plot of $\log(J(t))$ vs. $\log(t)$, where $J(t)$ is creep compliance and t is creep time. If the slope of the linear regression is greater than 0.97, steady state is considered to be reached, then the creep test is stopped. In all cases in this study the slope meets the criterion within 2 hours. The steady state shear rate is determined from the slope of the linear regression of all of the data points in the last 10% time window of the plot of ϵ vs. t , where ϵ is strain. The zero-shear viscosity is determined from the ratio of the applied stress to the steady state shear rate.

25

In order to determine if the sample is degraded during the creep test, a small amplitude oscillatory shear test is conducted before and after the creep test on the same specimen from 0.1 to 100 rad/s. The complex viscosity values of the two tests are compared. If the difference of the viscosity values at 0.1 rad/s is greater than 5%, the sample is considered to have degraded during the creep test, and the result is discarded.

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ZSVR definition:

Zero-shear viscosity ratio (ZSVR) is defined as the ratio of the zero-shear viscosity (ZSV) of the branched polyethylene material to the ZSV of the linear polyethylene material at the equivalent weight average molecular weight (Mw-gpc) as shown in the equation below.

$$ZSVR = \frac{\eta_{0B}}{\eta_{0L}} = \frac{\eta_{0B}}{2.29^{-15} M_{w-gpc}^{3.65}}$$

The ZSV value is obtained from creep test at 190oC via the method described above. The Mw-gpc value is determined by the conventional GPC method as described above. The correlation between ZSV of linear polyethylene and its Mw-gpc was established based on a series of linear polyethylene reference materials. A description for the ZSV-Mw relationship can be found in the ANTEC proceeding: Karjala, Teresa P.; Sammler, Robert L.; Mangnus, Marc A.; Hazlitt, Lonnie G.; Johnson, Mark S.; Hagen, Charles M., Jr.; Huang, Joe W. L.; Reichel, Kenneth N. Detection of low levels of long-chain branching in polyolefins. Annual Technical Conference - Society of Plastics Engineers (2008), 66th 887-891.

1H NMR method

3.26 g of stock solution is added to 0.133 g of polyolefin sample in 10 mm NMR tube. The stock solution is a mixture of tetrachloroethane-d2 (TCE) and perchloroethylene (50:50, w:w) with 0.001M Cr3+. The solution in the tube is purged with N2 for 5 minutes to reduce the amount of oxygen. The capped sample tube is left at room temperature overnight to swell the polymer sample. The sample is dissolved at 110oC with shaking. The samples are free of the additives that may contribute to unsaturation, e.g. slip agents such as erucamide.

The 1H NMR are run with a 10 mm cryoprobe at 120oC on Bruker AVANCE 400 MHz spectrometer.

Two experiments are run to get the unsaturation: the control and the double presaturation experiments.

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For the control experiment, the data is processed with exponential window function with LB=1 Hz, baseline was corrected from 7 to -2 ppm. The signal from residual 1H of TCE is set to 100, the integral Itotal from -0.5 to 3 ppm is used as the signal from whole polymer in the control experiment. The number of CH2 group,

5 NCH2, in the polymer is calculated as following:

$$NCH2=Itotal/2$$

For the double presaturation experiment, the data is processed with
 10 exponential window function with LB=1 Hz, baseline was corrected from 6.6 to 4.5 ppm. The signal from residual 1H of TCE is set to 100, the corresponding integrals for unsaturations (Ivinylene, Itrisubstituted, IvinyI and Ivinylidene) were integrated based on the region shown in the following Figure. The number of unsaturation unit for vinylenes, trisubstituted, vinyl and vinylidene are calculated:

15

$$Nvinylene=Nvinylene/2$$

$$Ntrisubstituted=Itrisubstitute$$

$$Nvinyl=Ivinyl/2$$

$$Nvinylidene=Ivinylidene/2$$

20

The unsaturation unit/ 1,000,000 carbons is calculated as following:

$$Nvinylene/1,000,000C = (Nvinylene/NCH2)*1,000,000$$

$$Ntrisubstituted/1,000,000C = (Ntrisubstituted/NCH2)*1,000,000$$

25 $Nvinyl/1,000,000C = (Nvinyl/NCH2)*1,000,000$

$$Nvinylidene/1,000,000C = (Nvinylidene/NCH2)*1,000,000$$

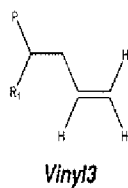
The requirement for unsaturation NMR analysis includes: level of quantitation
 30 is $0.47 \pm 0.02/1,000,000$ carbons for Vd2 with 200 scans (less than 1 hour data acquisition including time to run the control experiment) with 3.9 wt% of sample (for Vd2 structure, see Macromolecules, vol. 38, 6988, 2005), 10 mm high temperature cryoprobe. The level of quantitation is defined as signal to noise ratio of 10.

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The chemical shift reference is set at 6.0 ppm for the ^1H signal from residual proton from TCT-d2. The control is run with ZG pulse, TD 32768, NS 4, DS 12, SWH 10,000 Hz, AQ 1.64s, D1 14s. The double presaturation experiment is run with a modified pulse sequence , O1P 1.354 ppm, O2P 0.960 ppm, PL9 57db, PL21 70 db, 5 TD 32768, NS 200, DS 4, SWH 10,000 Hz, AQ 1.64s, D1 1 s, D13 13s.

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Group	Structure	Notation
Vinylene		Vinylene1
		Vinylene2
		Vinylene3
		Trisubstituted
		Trisubstituted
Vinyl		Vinyl1
		Vinyl2
Vinylidene		Vinylidene1
		Vinylidene2
		Vinylidene3



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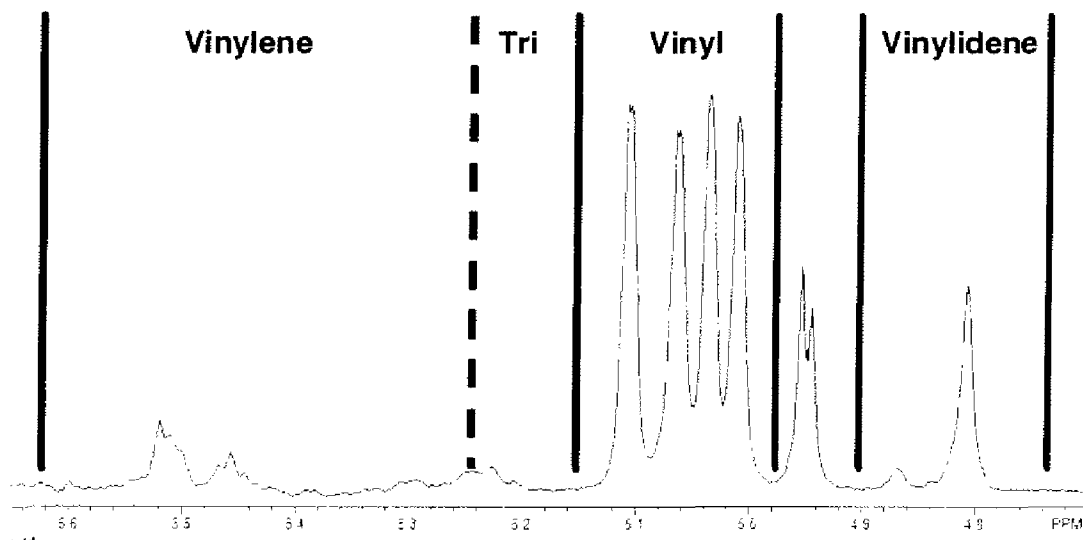
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1 ze
  d12 pl21:f2
2 30m
  d13
  d12 pl9:f1
  d1 cw:f1 ph29 cw:f2 ph29
  d11 do:f1 do:f2
  d12 pl1:f1
  p1 ph1
  go=2 ph31
  30m mc #0 to 2 F0(zd)
exit

ph1=0 2 2 0 1 3 3 1
ph29=0
ph31=0 2 2 0 1 3 3 1

```

Fig1
posi

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Gel Content

Gel content is determined in accordance to ASTM D2765-01 Method A in xylene. The sample is cut to required size using a razor blade.

5

Film Testing Conditions

The following physical properties are measured on the films produced:

- Total (Overall), Surface and Internal Haze: Samples measured for internal haze and overall haze are sampled and prepared according to ASTM D 1003. Internal haze was obtained via refractive index matching using mineral oil on both sides of the films. A Hazegard Plus (BYK-Gardner USA; Columbia, MD) is used for testing. Surface haze is determined as the difference between overall haze and internal haze as shown in Equation 2. Surface haze tends to be related to the surface roughness of the film, where surface increases with increasing surface roughness. The surface haze to internal haze ratio is the surface haze value divided by the internal haze value as shown in Equation 3.

10

15

$$\text{Haze} = \text{Internal Haze} + \text{Surface Haze} \quad (\text{Eq. 2})$$

$$S/I = \text{Surface Haze/Internal Haze} \quad (\text{Eq. 3})$$

- 45° Gloss: ASTM D-2457.
- MD and CD Elmendorf Tear Strength: ASTM D-1922
- MD and CD Tensile Strength: ASTM D-882
- Dart Impact Strength: ASTM D-1709
- Puncture Strength: Puncture is measured on a Instron Model 4201 with Sintech Testworks Software Version 3.10. The specimen size is 6" x 6" and 4 measurements are made to determine an average puncture value. The film is conditioned for 40 hours after film production and at least 24 hours in an ASTM controlled laboratory. A 100 lb load cell is used with a round specimen holder 12.56" square. The puncture probe is a 1/2" diameter polished stainless steel ball with a 7.5" maximum travel length. There is no gauge

25

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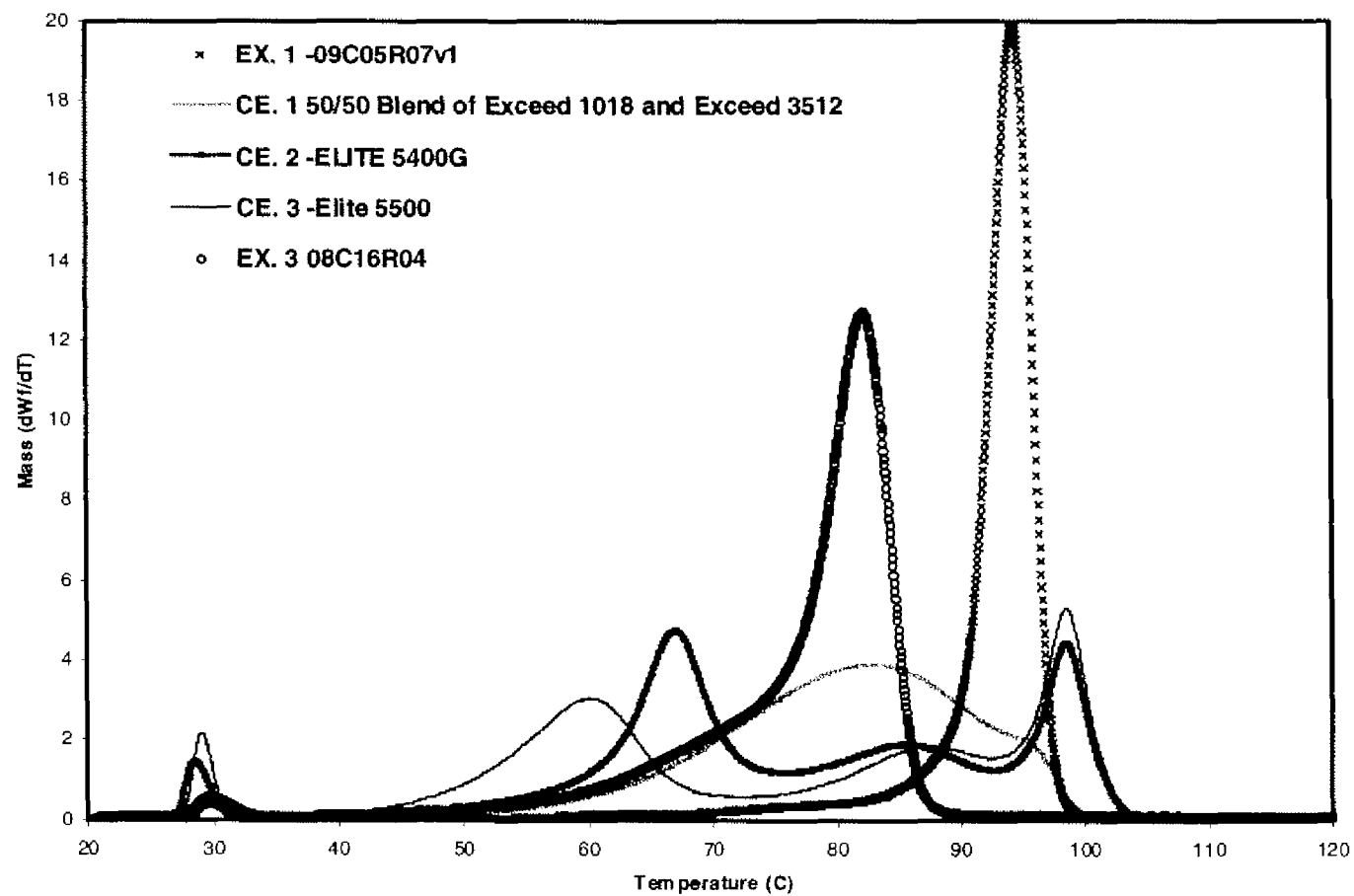
length; the probe is as close as possible to, but not touching, the specimen. The crosshead speed used is 10"/minute. The thickness is measured in the middle of the specimen. The thickness of the film, the distance the crosshead traveled, and the peak load are used to determine the puncture by the software.

- 5 The puncture probe is cleaned using a "Kim-wipe" after each specimen.

		Density (g/cc)	I10 (g/10min)	I2 (g/10min)	I10 / I2
EX 1	08C16R05	0.912	11.5	1.5	7.7
EX 2	09C05R07v1	0.937	7.1	0.4	16.1
CE 1	50/50 Blend Exceed 1018 and Exceed 3512	0.916	9.1	1.6	5.9
CE 2	ELITE 5400G	0.916	8.5	1.0	8.4
CE 3	ELITE 5500G	0.914	11.2	1.5	7.3
EX 3	08C16R04	0.912	11.5	1.6	7.4

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		Unsaturation Unit / 1,000,000 C				
		vinylene	trisubstituted	vinyl	vinylidene	Total
Ex. 1	08C16R05	6	2	47	7	62
Ex. 2	09C05R07 VI	5	1	59	6	71
CE 1	50/50 blend of Exceed 1018 and Exceed 3512	21	46	54	24	145
CE 2	ELITE 5400G	52	51	171	40	314
CE 3	ELITE 5500	41	32	149	30	252
Ex. 3	08C16R04	9	2	55	12	78

ID		Comonomer dist.Index	Stdev, C	HalfWidth, C	HalfWidth/Stdev	CDC(Comonomer Dist. Constant)
Ex. 1	08C16R05	0.873	12.301	16.823	1.368	63.8
Ex. 2	09C05R07 VI	0.838	6.250	3.721	0.595	140.9
CE 1	50/50 Blend of Exceed 1018 and Exceed 3512	0.662	10.508	25.270	2.405	27.5
CE 2	ELITE 5400G	0.515	18.448	36.739	1.991	25.9
CE 3	ELITE 5500	0.246	27.884	42.670	1.530	16.1
Ex. 3	08C16R04	0.802	11.003	5.788	0.526	152.4

CE 1 = 50/50 Blend of Exceed 1018, an ethylene/ hexene copolymer having I_2 of 1 g/10 minutes and density of 0.918 g/cm³ and Exceed 3512, an ethylene/ hexene copolymer having I_2 of 3.5 g/10 minutes and density of 0.912 g/cm³

CE 2 = ELITE 5400G, an ethylene/octene copolymer having I_2 of 1 g/10 minutes and density of 0.916 g/cm³.

CE 3 = ELITE 5500, an ethylene/octene copolymer having I_2 of 1.5 g/10 minutes and density of 0.914 g/cm³.

DSC Sample		Cool Curve Data		Heat Curve Data	
		Tc (C)	DeltaH cryst (J/g)	Tm (C)	DeltaH melt (J/g)
CE 2	ELITE 5400	105.1	141.6	123.63	143
CE 3	ELITE 5500	106.55	137.5	124	137.4
Ex. 3	08C16R04	93.97	130.4	108.33	131.7
Ex. 1	08C16R05	95.21	130.7	110.82	132.2
Ex. 2	09C05R07VI	112.97	179.6	123.79	178.4
CE 1	50% EXCEED 1018 50% EXCEED 3512	103.92	126.7	117.55	129.5

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			Conventional GPC		
	Identification	Mn	Mw	Mz	Mw/Mn
EX 1	08C16R05	32,370	86,200	170,500	2.7
EX 2	09C05R07v1	14,630	103,100	282,600	7.0
CE 1	50/50 BLEND OF EXCEED 1018 AND EXCEED 3512	36,780	95,950	174,500	2.6
CE 2	ELITE 5400G RESIN	24,600	101,900	238,200	4.1
CE 3	ELITE 5500G RESIN	28,800	105,100	374,900	3.6
EX 3	08C16R04	33,750	84,080	159,600	2.5

Shear Rate (1/sec) @ 190C		G' (Pa)				G'' (Pa)				Eta* (Pa-s)			
		0.1	1	10	100	0.1	1	10	100	0.1	1	10	100
EX 1	08C16R05	66	1221	12621	85376	620	4696	27476	102830	6240	4852	3024	1337
EX 2	09C05R07VI	1764	7855	30375	111000	2756	9716	33986	87314	32724	12494	4558	1412
CE 1	EXCEED 1018 / 3212	8	270	8214	97443	378	3670	29450	128860	3781	3679	3057	1616
CE 2	ELITE 5400	199	2134	18203	102500	957	6275	32869	104710	9775	6628	3757	1465
CE 3	ELITE 5500	34	892	11631	86949	529	4404	27610	104400	5296	4493	2996	1359
EX 3	08C16R04	52	1054	11539	84139	569	4411	26910	103850	5716	4535	2928	1337

Film Fabrication:

All resins are blown into monolayer films produced on a Collin three layers blown film line. The blown film line consists of three groove fed extruders with single flight screws (25:30:25mm). The length/diameter (L/D) ratio for all screws is 25:1. The blown film line has a 60mm die with dual lip air ring cooling system, with a screen pack configuration of 20:40:60:80:20 mesh. All films are produced at 1mil thickness.

		EX 1		CE 2		CE 3		EX 3	
		08C16R05		ELITE 5400		ELITE 5500		08C16R04	
Parameter	Unit								
Actual Speed	m/min	17.3		22.2		17.4		17.3	
Actual Rate	kg/hr	27.6		10.9		13.2		14.7	
Motor Load	Amp	6		6		6		6	
Screw Speed	rpm	50		50		50		50	
Pressure	Bar	289		306		300		287	
Melt Temperature	C	186		NA*		185		185	
Layflat width	cm	23.8		23.5		23.8		23.8	
Temperature profile		Set	Actual	Set	Actual	Set	Actual	Set	Actual
Core Barrel 1	C	180	180	170	170	180	180	180	180
Core Barrel 2	C	195	196	220	220	195	195	195	194
Core Barrel 3	C	190	189	175	175	190	189	190	189
Core Barrel 4	C	190	189	175	175	190	191	190	191
Adapter Temp	C	210	210	225	225	210	210	210	210
Tube	C	210	210	225	225	210	210	210	210
Die Temp 5	C	210	210	225	225	210	210	210	210
Die Temp 4	C	210	210	225	225	210	210	210	210
Die Temp 3	C	210	210	225	225	210	210	210	210
Die Temp 2	C	210	210	225	226	210	210	210	210
Die Temp 1	C	210	210	225	225	210	210	210	210
Die Gap	mil	2		2		2		2	
Frost Line	Inch	7		7		7		7	
BUR		2.5		2.5		2.5		2.5	

NA* - instrumentation failure

	EX 1 08C16R05	CE 2 Elite 5400	CE 3 Elite 5500	EX 3 08C16R04
Gloss 45 deg (%)	76	78	91	83
Haze - Film (%)	7	6	4	5
Haze - Internal (%)	0.6	1.3	1.3	0.5
Dart A (g)	850	850	703	850
Dart B (g)	580	666	-	676
Elmendorf Tear MD Normalized (g/mil)	334	256	376	378
Elmendorf Tear CD Normalized (g/mil)	465	535	614	521
PUNCTURE (ft*lb/in ³)	237	399	146	342
Tensile - CD Break Stress (psi)	6336	7039	6419	6811
Tensile - CD Energy to Break (in*lb)	32	33	34	34
Tensile - CD Strain at Break (%)	641	678	666	670
Tensile - CD Stress at Yield (psi)	1419	1595	1477	1404
Tensile - MD Break Stress (psi)	6830	7320	7046	7417
Tensile - MD Energy to Break (in*lb)	26	24	30	28
Tensile - MD Strain at Break (%)	476	436	525	506
Tensile - MD Stress at Yield (psi)	1713	1607	1654	1684

	Resins					
for sealant layer	CE 3. ELITE 5500G + slip + AB	96.75% ELITE 5500G	2.0% slip (in LDPE)	1.25% AB (in LDPE)	1000 ppm slip (LDPE based)	2500 ppm AntiBlock (LDPE based)
	EX 3. 08C16R04 + slip + AB	96.75% 08C16R04	2.0% slip (in LDPE)	1.25% AB (in LDPE)	1000 ppm slip (LDPE based)	2500 ppm AntiBlock (LDPE based)
	EX 1. 08C16R05 + slip + AB	96.75% 08C16R05	2.0% slip (in LDPE)	1.25% AB (in LDPE)	1000 ppm slip (LDPE based)	2500 ppm AntiBlock (LDPE based)

	Resins					
for skin layer	DOWLEX 2045.11G	96.1% DOWLEX 2045G	2.4% slip (in LDPE)	1200 ppm slip (LDPE based)	3000 ppm AntiBlock (LDPE based)	
for core layer	75% DOWLEX 2045G + 25% INSPIRE 114 PP + slip + AB	72.1% DOWLEX 2045G	2.4% slip (in LDPE)	1200 ppm slip (LDPE based)	3000 ppm AntiBlock (LDPE based)	

Slip= 1200 ppm Erucamide (slip) in LDPE carrier resin 5% loading. 1.2E-3 ppm amount active ingredient in final product. 2.4% amount additive in final product

AB= 3000 ppm DE (diamatious earth-antiblock) in LDPE carrier resin 20% loading. 3.0E-3 ppm amount active ingredient in final product. 1.5% amount additive in final product

1000 ppm Erucamide (slip) in LDPE carrier resin 5% loading. 1.0E-3 ppm amount active ingredient in final product. 2.0% amount additive in final product

2500 ppm DE (diamatious earth-antiblock) in LDPE carrier resin 20% loading. 2.5E-3 ppm amount active ingredient in final product. 1.25% amount additive in final product

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Film Fabrication:

Three layer co-ex films are fabricated on a three layer co-extruded blown film line consisting of two 2.5 inch 24:1 L/D Egan extruders (Extruders A and B) and one 2 inch 24:1 L/D Johnson extruder (Extruder C). All the extruders are smooth bore with barrel heating and cooling (closed loop liquid cooling system). The extruders are powered by 60, 75, and 20 HP DC drives, respectively. The extruders are controlled by an Extrol 6032 microprocessor. The extrusion process is monitored by Pressure Transducers, three on the 2 1/2" barrels, one before and one after each breaker plate as well as 4 heater zones on each barrel, one each at the adapter and the block and two zones on the die. The Microprocessor also tracks the extruder RPM, % FLC, HP, Rate, Layflat and melt temperature at each extruder.

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- 5 The die is a 6 inch Battenfeld-Gloucester with a layer ratio of 15:75:15% and a 70mil die gap. The standard screws used are New Castle's single flight high shear screws with a 2.88 compression ratio on Extruder A, Feed Screw's Modified Double mix with a 3.64 compression ratio on Extruder B, and Johnson single flight with a 2.5 compression ratio on Extruder C. Co-ex film structure of 2.5 mil film (1.0 mil sealant / 1.0 mil core / 0.5 mil skin layer), slit to 21.5", cut flush with core, was produced at a 2.5:1 BUR. The screen pack configuration was 20:40:60:80:20 mesh.

EX 5

	08C16R04 Ex. 3			2046G +D114		DOWLEX 2045.11	
Parameter							
Actual Speed	Unit	47.2		48.1		29.5	
Actual Rate	lb/hr	63.6		64		32.4	
Layer ratio	%	40		40		20	
%FLC		56.9		37.1		15.3	
HP		13		7		2	
Pressure 1	psi	-		1060		-	
Pressure 2	psi	2050		1230		-	
Pressure 3	psi	5780		2700		-	
Screen Pressure	psi	5310		-		4200	
Adaptor pressure	psi	4170		2480		3500	
Melt Temperature	F	422		425		414	
Layflat width	Cm	60		60		60	
	Layer A			Layer B		Layer C	
Temperature profile		Set	Actual	Set	Actual	Set	Actual
Barrel 1	F	375	375	375	375	375	377
Barrel 2	F	425	425	425	425	425	426
Barrel 3	F	380	380	380	383	400	400
Barrel 4	F	380	377	380	381	400	400
Adapter	F	400	400	400	400	420	420
Block	F			450	446		
Lower Die	F			450	450		
Upper Die	F			450	450		
Inner Die				450	450		
External Air Temp	C			45	45		
Internal Air Temp	C			45	75		
Die Gap	mil			70			
Overall Speed	Unit			53.6			
Overall Rate	lb/hr			160			
BUR				2.5			

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		EX 4			CE 4		
		08C16R05 Ex. 1	2045G +D114	DOWLEX 2045.11	ELITE 5500G CE.3	2045G +D114	DOWLEX 2045.11
Parameter							
Actual Speed	Unit	48.2	47.6	29.1	50.1	48.5	29.5
Actual Rate	lb/hr	64.4	64.3	32.1	63.5	64.3	32.5
Layer ratio	%	40	40	20	40	40	20
%FLC		57.7	36.5	15.2	58.2	37.3	15.6
HP		13	7	2	14	7	2
Pressure 1	psi	-	1130	-	-	1080	-
Pressure 2	psi	2570	1490	-	1950	1120	-
Pressure 3	psi	5500	2720	-	5750	2750	-
Screen Pressure	psi	5460	-	4120	5460	-	4260
Adaptor pressure	psi	4260	2470	3450	4380	2530	3540
Melt Temperature	F	426	424	415	425	425	413
Layflat width	Cm	60	60	60	60	60	60
		Layer A		Layer B	Layer C		
Temperature profile		Set	Actual	Set	Actual	Set	Actual
Barrel 1	F	375	376	375	375	375	374
Barrel 2	F	425	425	425	426	425	425
Barrel 3	F	380	382	380	376	400	400
Barrel 4	F	380	385	380	383	400	400
Adapter	F	400	400	400	399	420	420
Block	F			450	448		
Lower Die	F			450	450		
Upper Die	F			450	450		
Inner Die				450	450		
External Air Temp	C			45	45		
Internal Air Temp	C			45	75		
Die Gap	mil			70			
Overall Speed	Unit			50.8			
Overall Rate	lb/hr			161			
BUR				2.5			

- Films are evaluated on a Weigh Pack Systems XPDIUS ELITE series VFS bagger. The Weigh Pack VFFS packaging equipment used poly sealing jaws: false jaws + seal jaws, where the seal jaws back is concave and the front is jaw is convex. The catch plates are V-shaped just above seal jaws. The jaw strength is set at 180 units, based on the servo motor. The fin seal jaw is set at 50 psi dwell pressure.
- Bags are tested using 2 lbs of measured dry red beans as the fill product. Pre-measured 2 lbs amounts of dry red beans are poured by hand into the VFFS bags via the forming collar. Products are evaluated for minimum seal temperature and minimum dwell time, two critical parameters for maximization of VFFS production rate. The minimum seal temperature is determined by filling the VFFS bags with 2 lbs worth of dried beans at a constant dwell time (1.35 s) and lowering the seal temperature until the VFFS bags would no longer hold the dried beans. To determine the minimum dwell time pillow pouches are made (VFFS bags with no product). The tests are started at 5 deg C above the minimum seal temperature required to hold 2 lbs of dried beans. The seal bar dwell time is then shortened until the VFFS bag would no longer hold a seal.

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- For the minimum seal temperature determination, after the packages are made they are allowed to "setup" for approximately 30 seconds and then vigorously shook to make sure the content held for the 2 lb bean packages. For the minimum dwell temperature
- 5 determination the air-filled-only pillow pouches are allowed to setup for approximately 30 second to allow the seal to set-up and then hand pressure is applied to the packages to make sure they would not burst open at the seal or have a large "channel" leaker. A channel leaker is a large hole formed at the point where either of the seals on the ends of the package overlapped with long seal on the long-edge of the package. A hermetic (air-
- 10 tight) seal is not required for most solid food applications, including frozen foods.

Film	Minimum Seal Temp 2 lb fill weight / 1.35 seconds dwell time		Minimum dwell time Air fill / Min. fill temp	
	HTIT (C)	dwell time (s)	HTIT (C)	dwell time (s)
CE 4. ELITE 5500G	Fail	Fail	140	2
	<i>(Only 1lb fill / still couldn't hold product)</i>			
EX 5. 08C16R04	130	1.35	135	1.15
EX 4. 08C16R05	135	1.35	135	1.25

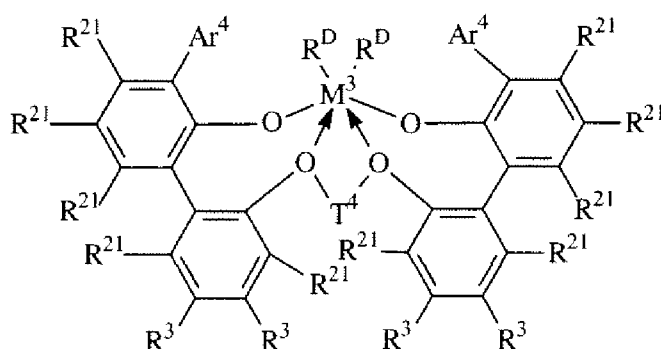
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We claim:

1. An ethylene-based polymer composition characterized by a Comonomer
Distribution Constant greater than about 45, more preferably greater than 50,
5 most preferably greater than 95, and as high as 400, preferably as high as 200,
wherein the composition has less than 120 total unsaturation unit/1,000,000C.
2. The polymer composition of Claim 1 wherein the composition comprises up to
about 3 long chain branches/1000 carbons, preferably from about 0.01 to
10 about 3 long chain branches/1000 carbons.
3. The polymer composition of claim 1 having a ZSVR of at least 2.
4. The polymer of claim 3 further characterized by comprising less than 20
15 vinylidene unsaturation unit/1,000,000C.
5. The polymer composition of Claim 1 where in the composition has a bimodal
molecular weight distribution.
- 20 6. The polymer composition of Claim 1 where in the composition has a multi-
modal MWD.
7. A fabricated article comprising the composition of Claim 1.
- 25 8. The polymer composition of claim 1 further comprising a single DSC melting
peak.
9. A thermoplastic formulation comprising the composition of claim 1 and at
least one natural or synthetic polymer.
- 30 10. The composition of claim 1, wherein said composition has been at least
partially cross-linked (at least 5% gel).

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11. The composition of claim 1 wherein the composition has a comonomer distribution profile comprising a mono or bimodal distribution from 35°C to 120°C, excluding purge.
- 5 12. The polymer composition of claim 1 comprising Mw from about 17,000 to about 220,000.
13. A polymerization process comprising:
- (A) polymerizing ethylene, and, optionally a C₃-C₂₀ alpha-olefin, in the presence of a first catalyst to form a semi-crystalline ethylene-based polymer in a first reactor or a first part of a multi-part reactor; and
- 10 (B) reacting the semi-crystalline ethylene-based polymer with additional ethylene in the presence of a second catalyst to form an ethylenic polymer in at least one other reactor or a later part of a multi-part reactor, wherein the catalyst of (A) and
- 15 (B) can be the same or different and each catalyst of (A) and (B) is a metal complex of a polyvalent aryloxyether corresponding to the formula:



where M³ is Ti, Hf or Zr, preferably Zr;

- 20 Ar⁴ independently each occurrence is a substituted C₉₋₂₀ aryl group, wherein the substituents, independently each occurrence, are selected from the group consisting of alkyl; cycloalkyl; and aryl groups; and halo-, trihydrocarbylsilyl- and halohydrocarbyl- substituted derivatives thereof, with the proviso that at least one substituent lacks co-planarity with the aryl group to which it is attached;
- 25 T⁴ independently each occurrence is a C₂₋₂₀ alkylene, cycloalkylene or cycloalkenylene group, or an inertly substituted derivative thereof;

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R^{21} independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbysilyl, trihydrocarbysilylhydrocarbyl, alkoxy or di(hydrocarbyl)amino group of up to 50 atoms not counting hydrogen;

- R^3 independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbysilyl, trihydrocarbysilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen, or two R^3 groups on the same arylene ring together or an R^3 and an R^{21} group on the same or different arylene ring together form a divalent ligand group attached to the arylene group in two positions or join two different arylene rings together; and

- R^D , independently each occurrence is halo or a hydrocarbyl or trihydrocarbysilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl, diene, or poly(hydrocarbyl)silylene group, especially where the reaction of step (B) occurs by graft polymerization.

14. The fabricated article of claim 8 in the form of at least one film layer.

15. A method of characterizing an ethylene based polymer for comonomer composition distribution (CDC) comprising the following steps:
(A) Obtain a weight fraction at each temperature (T) ($w_T(T)$) from 35.0°C to 119.0°C with a temperature step of 0.200°C from CEF according Equation 2,

$$\int_{35}^{119.0} w_T(T) dT = 1 \dots \dots \text{Equation 2}$$

- (B) Calculate the mean temperature (T_{mean}) at cumulative weight fraction of 0.500 (Equation 3),

$$\int_{35}^{T_{mean}} w_T(T) dT = 0.5 \dots \dots \dots \text{Equation 3}$$

- (C) Calculate the corresponding median comonomer content in mole % (C_{median}) at the median temperature (T_{median}) by using comonomer content calibration curve (Equation 4),

$$\ln(1 - \text{comonomer content}) = -\frac{207.26}{273.12 + T} + 0.5533 \dots \dots \text{Equation 4}$$

$$R^2 = 0.997$$

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(D) Construct a comonomer content calibration curve by using a series of reference materials with known amount of comonomer content, eleven reference materials with narrow comonomer distribution (mono modal comonomer distribution in CEF from 35.0 to 119.0°C) with weight average Mw of 35,000 to 115,000 (by conventional GPC) at a comonomer content ranging from 0.0 mole% to 7.0mole% are analyzed with CEF at the same experimental conditions specified in CEF experimental sections.

(E) Calculate comonomer content calibration by using the peak temperature (T_p) of each reference material and its comonomer content, the calibration is: R^2 is the correlation constant,

(F) Calculate Comonomer Distribution Index from the total weight fraction with a comonomer content ranging from $0.5 * C_{median}$ to $1.5 * C_{median}$, if T_{median} is higher than 98.0°C, Comonomer Distribution Index is defined as 0.95,

(G) Obtain Maximum peak height from CEF comonomer distribution profile by searching each data point for the highest peak from 35.0°C to 119.0°C (if the two peaks are identical then the lower temperature peak is selected), half width is defined as the temperature difference between the front temperature and the rear temperature at the half of the maximum peak height, the front temperature at the half of the maximum peak is searched forward from 35.0°C, while the rear temperature at the half of the maximum peak is searched backward from 119.0°C, in the case of a well defined bimodal distribution where the difference in the peak temperatures being equal to or larger than the sum of half width of each peak, the half- width of the polymer is calculated as the arithmetic average of the half width of each peak.

(H) Calculate the standard deviation of temperature ($Stdev$) according Equation 5:

$$Stdev = \sqrt{\sum_{35.0}^{119.0} (T - T_p)^2 * w_T(T)} \dots \dots \text{Equation 5}$$