



(51) International Patent Classification:

C08F 10/02 (2006.01) C08J 5/18 (2006.01)
C08F 2/00 (2006.01) C08L 23/04 (2006.01)

(21) International Application Number:

PCT/US2013/029652

(22) International Filing Date:

7 March 2013 (07.03.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/706,936 28 September 2012 (28.09.2012) US

(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC**
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors: **KARJALA, Teresa, P.**; 56 Mandevilla Court,
Lake Jackson, TX 77566 (US). **KARDOS, Lori, L.**; 15
Sarahs Cove, Sugar Land, TX 77479 (US). **YAU, Wallace,
W.**; 12208 Hidden River Lane, Pearland, TX 77584 (US).
ORTEGA, Jose; 202 Beechwood, Lake Jackson, TX
77566 (US).

(74) Agent: **TERRY, Jane**; The Dow Chemical Company, P.O.
Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ETHYLENE-BASED POLYMERS AND PROCESSES TO MAKE THE SAME

(57) Abstract: The invention provides a composition comprising a low density polyethylene (LDPE) obtained by free radical polymerization of ethylene, and wherein the LDPE has a GPC-Viscometer parameter "DPP" less than 1.3. The invention also provides a composition comprising an ethylene-based polymer that comprises the following features: a) at least 0.1 amyl groups per 1000 total carbon atoms; b) a melt index from 0.5 to 0.9 c) a MWD(conv) [(Mw(conv)/Mn(conv))] from 9 to 13; The invention also provides a composition comprising an ethylene-based polymer that comprises the following features: a) at least 0.1 amyl groups per 1000 total carbon atoms; b) a MWD(conv) from 9 to 13; c) a gpcBR value from 2.0 to 5.0; d) a melt strength (MS) greater than 20 cN.



WO 2014/051675 A1

ETHYLENE-BASED POLYMERS AND PROCESSES TO MAKE THE SAME

REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Application No.
5 61/706,936, filed September 28, 2012.

BACKGROUND OF THE INVENTION

Blown film production lines are typically limited in output by bubble stability.
Blending Linear Low Density Polyethylene (LLDPE) with 0.5 wt% to 90 wt% of Low
10 Density Polyethylene (LDPE) increases bubble stability, in part, due to the higher melt
strength of the LDPE. The increase in melt strength, in part, provides for an increase in film
output. However, too high a melt strength can cause gels and poor quality film, as well as
potentially limiting drawdown capabilities to thinner gauges (0.5 to 1 mil film). High melt
strength resins also typically have reduced toughness properties. Thus, there is a need for
15 new ethylene-based polymers, such as LDPEs, that have an optimized balance of melt
strength and improved film mechanical properties, for blown film applications.

LDPE polymers are disclosed in the following references: WO 2010/042390, WO
2010/144784, WO 2011/019563, WO 2012/082393, WO 2006/049783, WO 2009/114661,
US 2008/0125553, U.S. 7741415, and EP 2239283B1. However, such polymers do not
20 provide an optimized balance of high melt strength and improved film mechanical properties,
for blown film applications. Thus, as discussed above, there remains a need for new
ethylene-based polymers, such as LDPEs, that have an optimized balance of melt strength,
optics, processability and output, and toughness. These needs and others have been met by
the following invention.

25

SUMMARY OF THE INVENTION

The invention provides a composition comprising a low density polyethylene (LDPE)
obtained by free radical polymerization of ethylene, and wherein the LDPE has a GPC-
Viscometer parameter "DPP" less than 1.3.

30 The invention also provides a composition comprising an ethylene-based polymer that
comprises the following features:

- a) at least 0.1 amyl groups per 1000 total carbon atoms;
- b) a melt index from 0.5 to 0.9
- c) a MWD(conv) [(Mw(conv)/Mn(conv))] from 9 to 13;

The invention also provides a composition comprising an ethylene-based polymer that comprises the following features:

- a) at least 0.1 amyl groups per 1000 total carbon atoms;
- b) a MWD(conv) from 9 to 13;
- 5 c) a gpcBR value from 2.0 to 5.0;
- d) a melt strength (MS) greater than 20 cN.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts a GPC-DP (differential pressure viscometer) profile of Example 1.

10 Figure 2 depicts a GPC- DP (differential pressure viscometer) profile of Example 2.

Figure 3 depicts a GPC- DP (differential pressure viscometer) profile of Comparative Example 1.

Figure 4 depicts a block diagram of the process reaction system used to produce the Inventive Examples.

15

DETAILED DESCRIPTION

Novel ethylene-based polymers, such as LDPEs, were developed, with optimized melt strength, to increase processability and output; allow drawability to thin gauges; minimize gels when blended with other polymers, and improve toughness relative to current LDPE products.

20

As discussed above, in a first aspect, the invention provides a composition comprising a low density polyethylene (LDPE) obtained by free radical polymerization of ethylene, and wherein the LDPE has a GPC-Viscometer parameter "DPP" less than 1.3.

25

The composition may comprise a combination of two or more embodiments as described herein.

The LDPE may comprise a combination of two or more embodiments as described herein.

In one embodiment, the LDPE has a GPC-Viscometer parameter "DPP" less than 1.5, further less than 1.3, and further less than 1.2.

30

In one embodiment, the LDPE has a GPC-Viscometer parameter "DPP" less than 1.3, further less than 1.25, and further less than 1.2.

In one embodiment, the LDPE has a GPC-Viscometer parameter "DPP" from 0.3 to 1.3, further from 0.5 to 1.3, and further from 0.8 to 1.2.

In one embodiment, the LDPE has at least 0.1 amyl groups per 1000 total carbon atoms.

In one embodiment, the LDPE has a MWD(conv) $[Mw(conv)/Mn(conv)]$ from 8 to 13, further from 8.5 to 12.5, and further from 9 to 12..

5 In one embodiment, the LDPE has a melt strength greater than, or equal to, 20 cN, further greater than, or equal to, 22 cN, and further greater than, or equal to, 23 cN.

In one embodiment, the LDPE has a melt strength from 20 to 30 cN, further from 22 to 27 cN, and further from 23 to 25 cN.

10 The composition of any of the previous claims, wherein the LDPE has a melt strength of at least 22 cN and less than 27 cN, with a minimum velocity at break of 70 mm/s.

The composition of any of the previous claims, wherein the LDPE has a melt strength of at least 22 cN and less than 27 cN, with a velocity at break of less than, or equal to, 400 mm/s.

15 In one embodiment, the LDPE has a gpcBR value from 2.0 to 6.0, further from 2.5 to 5.5, and further from 3.0 to 5.0.

In a second aspect, the invention provides a composition comprising an ethylene-based polymer that comprises the following features:

- a) at least 0.1 amyl groups per 1000 total carbon atoms;
- b) a melt index from 0.5 to 0.9
- 20 c) a MWD(conv) $[(Mw(conv)/Mn(conv))]$ from 9 to 13;

In a third aspect, the invention provides a composition comprising an ethylene-based polymer that comprises the following features:

- a) at least 0.1 amyl groups per 1000 total carbon atoms;
- b) a MWD(conv) $[(Mw(conv)/Mn(conv))]$ from 9 to 13;
- 25 c) a gpcBR value from 2.0 to 5.0;
- d) a melt strength (MS) greater than 20 cN.

The following embodiments apply to both the second and third aspects of the invention.

30 The composition may comprise a combination of two or more embodiments as described herein.

The ethylene-based polymer may comprise a combination of two or more embodiments as described herein.

In one embodiment, the ethylene-based polymer has a GPC-Viscometer parameter "DPP" less than 2.0, further less than 1.8, and further less than 1.6.

In one embodiment, the ethylene-based polymer has a melt strength greater than, or equal to, 22 cN, and further greater than, or equal to, 23 cN.

In one embodiment, the ethylene-based polymer has a melt strength from 20 to 30 cN, further from 22 to 27 cN, and further from 23 to 25 cN.

5 In one embodiment, the ethylene-based polymer has a gpcBR value from 2.5 to 5.0, and further from 3.0 to 5.0.

In one embodiment, the ethylene-based polymer has a MWD(conv) [Mw(conv)/Mn(conv)] from 9 to 13.5, and further from 9.5 to 12.

The following embodiments apply to all three aspects (compositions) of the invention.

10 In one embodiment, the polymer has a melt index (I2) from 0.01 to 10 g/10 min, further from 0.05 to 5 g/10 min, and further from 0.1 to 2 g/10 min.

In one embodiment, the polymer has a melt index (I2) from 0.1 to 1.5 g/10 min, further from 0.2 to 1.0 g/10 min, and further from 0.3 to 0.9 g/10 min.

In one embodiment, the polymer has a density from 0.910 to 0.940 g/cc, further from 15 0.910 to 0.930 g/cc, further from 0.915 to 0.925 g/cc, and further from 0.916 to 0.922 g/cc (1 cc = 1 cm³).

In one embodiment, the polymer has a cc-GPC Mw from 160,000 g/mol to 240,000 g/mol, further from 180,000 to 230,000 g/mol, and further from 200,000 g/mol to 220,000 g/mol.

20 In one embodiment, the polymer has a cc-GPC Mz from 680,000 to 890,000 g/mol, further from 700,000 g/mol to 830,000 g/mol, and further from 730,000 g/mol to 770,000 g/mol.

In one embodiment, the polymer has a Mw-abs from 550,000 g/mol to 930,000 g/mol, further from 580,000 g/mol to 830,000 g/mol, and further from 610,000 g/mol to 720,000 25 g/mol.

In one embodiment, the polymer has a Mw(LS-abs)/Mw(cc-GPC) from 3.04 to 3.60 and further from 3.05 to 3.40.

In one embodiment, the polymer has an IVw from 1.10 dl/g to 1.25 dl/g, and further from 1.15 dl/g to 1.25 dl/g.

30 In one embodiment, the polymer has an IVcc from 2.4 dl/g to 2.9 dl/g, and further from 2.5 to 2.8 dl/g.

In one embodiment, the polymer has an IVcc/IVw from 2.18 to 2.35, and further from 2.20 to 2.30.

In one embodiment, the polymer has greater than, or equal to, 0.2 amyl groups (branches) per 1000 carbon atoms, further greater than, or equal to, 0.5 amyl groups per 1000 carbon atoms, and further greater than, or equal to, 1 amyl groups per 1000 carbon atoms.

5 In one embodiment, the ethylene-based polymer has a rheology ratio ($V_{0.1} / V_{100}$), at 190°C, greater than, or equal to, 10, further greater than, or equal to, 20.

In one embodiment, the ethylene-based polymer has a rheology ratio ($V_{0.1} / V_{100}$), at 190°C, from 10 to 50, further from 20 to 40, and further from 25 to 35.

In one embodiment, the ethylene-based polymer has a tan delta (measured at 0.1 rad/s, 190°C) less than, or equal to 3.0, or less than, or equal to 2.5.

10 In one embodiment, the ethylene-based polymer has a viscosity at 0.1 rad/s, at 190°C, from 12,000 Pa•s to 19,000 Pa•s, further from 13,500 Pa•s to 18,900 Pa•s, and further from 15,000 Pa•s to 18,750 Pa•s.

In one embodiment, the ethylene-based polymer is formed in a high pressure (P greater than 100 MPa) polymerization process.

15 In one embodiment, the ethylene-based polymer is a low density polyethylene (LDPE).

In one embodiment, the ethylene-based polymer is a low density polyethylene (LDPE) formed by a high pressure (P greater than 100 MPa), free radical polymerization of ethylene.

20 In one embodiment, the ethylene-based polymer is present at greater than, or equal to, 10 weight percent, based on the weight of the composition.

In one embodiment, the ethylene-based polymer is present in an amount from 10 to 50 weight percent, further from 20 to 40 weight percent, based on the weight of the composition.

25 In one embodiment, the ethylene-based polymer is present in an amount from 60 to 90 weight percent, further from 65 to 85 weight percent, based on the weight of the composition.

In one embodiment, the ethylene-based polymer is present in an amount from 1 to 10 weight percent, further from 1.5 to 5 weight percent, based on the weight of the composition.

30 In one embodiment, the composition further comprises another ethylene-based polymer that differs in one or more properties, such as density, melt index, comonomer, comonomer content, etc., from the inventive ethylene-based polymer. Suitable other ethylene-based polymers include, but are not limited to, DOWLEX Polyethylene Resins, TUFLIN Linear Low Density Polyethylene Resins, ELITE or ELITE AT Enhanced Polyethylene Resins (all available from The Dow Chemical Company), high density polyethylenes ($d \geq 0.96$ g/cc), medium density polyethylenes (density from 0.935 to 0.955

g/cc), EXCEED polymers and ENABLE polymers (both from ExxonMobil), LDPE, and EVA (ethylene vinyl acetate).

In one embodiment, the composition further comprises a propylene-based polymer. Suitable propylene-based polymers include polypropylene homopolymers, propylene/ α -olefin
5 interpolymers, and propylene/ethylene interpolymers.

In one embodiment, the composition further comprises a heterogeneously branched ethylene/ α -olefin interpolymers, and preferably a heterogeneously branched ethylene/ α -olefin copolymer. In one embodiment, the heterogeneously branched ethylene/ α -olefin
10 interpolymers, and preferably a heterogeneously branched ethylene/ α -olefin copolymer, has a density from 0.89 to 0.94 g/cc, further from 0.90 to 0.93 g/cc. In a further embodiment, the composition comprises 1 to 99 weight percent, further from 15 to 85 weight percent, of the inventive ethylene-based polymer, based on the weight of the composition.

In one embodiment, the composition comprises less than 5 ppm, further less than 2 ppm, further less than 1 ppm, and further less than 0.5 ppm sulfur, based on the weight of the
15 composition.

In one embodiment, the composition does not contain sulfur.

In one embodiment, the composition comprises from 1.5 to 80 weight percent of an inventive ethylene-based polymer. In a further embodiment, the composition further
20 comprises a LLDPE (Linear Low Density Polyethylene).

In one embodiment, the composition comprises from 1.5 to 20 weight percent of an inventive ethylene-based polymer. In a further embodiment, the composition further
25 comprises a LLDPE.

In one embodiment, the composition comprises from 20 to 80 weight percent, further from 50 to 80 weight percent of an inventive ethylene-based polymer. In a further
30 embodiment, the composition further comprises a LLDPE.

An inventive composition may comprise a combination of two or more embodiments as described herein.

The invention also provides an article comprising at least one component formed from an inventive composition. In a further embodiment, the article is a film. In another
35 embodiment, the article is a coating.

The invention also provides a process for forming an inventive ethylene-based polymer of any of the previous embodiments, the process comprising polymerizing ethylene, and optionally at least one comonomer, in at least one autoclave reactor.

The invention also provides a process for forming a polymer of any of the previous embodiments, the process comprising polymerizing ethylene, and optionally at least one comonomer, in at least one tubular reactor.

5 The invention also provides a process for forming an inventive ethylene-based polymer of any of the previous embodiments, the process comprising polymerizing ethylene, and optionally at least one comonomer, in a combination of at least one tubular reactor and at least one autoclave reactor.

An inventive composition may comprise a combination of two or more embodiments as described herein.

10 An inventive ethylene-based polymer may comprise a combination of two or more embodiments as described herein.

An inventive LDPE may comprise a combination of two or more embodiments as described herein.

15 An inventive article may comprise a combination of two or more embodiments as described herein. An inventive film may comprise a combination of two or more embodiments as described herein.

An inventive process may comprise a combination of two or more embodiments as described herein.

Process

20 For producing an inventive ethylene-based polymer, a high pressure, free-radical initiated, autoclave polymerization process is typically used. The autoclave reactor normally has several injection points for initiator or monomer feeds, or both. The beginning of a reaction zone for the reactor is typically defined by the side injection of either initiator of the reaction, ethylene, chain transfer agent (or telomer), comonomer(s), as well as any
25 combination thereof. A high pressure process can also be carried out in a combination of autoclave and tubular reactors, each comprising one or more reaction zones. The high pressure polymerization may also be conducted in a tubular reactor.

A chain transfer agent can be used to control molecular weight. In a preferred embodiment, one or more chain transfer agents (CTAs) are added to an inventive
30 polymerization process. Typical CTAs include, but are not limited to, propylene, isobutane, n-butane, 1-butene, methyl ethyl ketone, acetone, and propionaldehyde. In one embodiment, the amount of CTA used in the process is from 0.03 to 10 weight percent of the total reaction mixture.

Ethylene used for the production of the ethylene-based polymer (e.g., LDPE) may be purified ethylene, which is obtained by removing polar components from a loop recycle stream, or by using a reaction system configuration, such that only fresh ethylene is used for making the inventive polymer. It is not typical that only purified ethylene is required to make
5 the ethylene-based polymer. In such cases ethylene from the recycle loop may be used.

In one embodiment, the ethylene-based polymer is a polyethylene homopolymer.

In another embodiment, the ethylene-based polymer comprises ethylene and one or more comonomers, and preferably one comonomer. Comonomers include, but are not limited to, α -olefin comonomers, typically having no more than 20 carbon atoms. For
10 example, the α -olefin comonomers may have 3 to 10 carbon atoms, further 3 to 8 carbon atoms. Exemplary α -olefin comonomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. In the alternative, exemplary comonomers include, but are not limited to α,β -unsaturated C3-
15 C8-carboxylic acids (for example, maleic acid, fumaric acid, itaconic acid, acrylic acid, methacrylic acid), crotonic acid derivatives of the α,β -unsaturated C3-C8-carboxylic acids (for example, unsaturated C3-C15-carboxylic acid esters, in particular ester of C1-C6-
alkanols, or anhydrides), methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methacrylic anhydride, maleic anhydride, and itaconic anhydride. In
20 another alternative, the exemplary comonomers include, but are not limited to, vinyl carboxylates, for example vinyl acetate. In another alternative, exemplary comonomers include, but are not limited to, n-butyl acrylate, acrylic acid and methacrylic acid.

Additives

An inventive composition may comprise one or more additives. Additives include,
25 but are not limited to, stabilizers, plasticizers, antistatic agents, pigments, dyes, nucleating agents, fillers, slip agents, fire retardants, processing aids, smoke inhibitors, viscosity control agents and anti-blocking agents. The 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 inventive polymer composition.

30 In one embodiment, the polymers of this invention are treated with one or more stabilizers, for example, antioxidants, such as IRGANOX 1010, IRGANOX 1076 and IRGAFOS 168 (Ciba Specialty Chemicals; Glattbrugg, Switzerland). In general, the polymers are treated with one or more stabilizers before extrusion or other melt processes. Processing aids, such as plasticizers, 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
5 371 naphthenic oil (Shell Lubricants; Houston, Tex.). One other suitable oil is TUFFLO oil (Lyondell Lubricants; Houston, Tex).

Blends and mixtures of the inventive polymer with other polymers may be performed. Suitable polymers for blending with the inventive polymer include natural and synthetic polymers. Exemplary polymers for blending include propylene-based polymers (both impact
10 modifying polypropylene, isotactic polypropylene, atactic polypropylene, and random ethylene/propylene copolymers), various types of ethylene-based polymers, including high pressure, free-radical LDPE, LLDPE prepared with Ziegler-Natta catalysts, PE prepared with single site catalysts, including multiple reactor PE (“in reactor” blends of Ziegler-Natta PE and single site catalyzed PE, such as products disclosed in USP 6,545,088 (Kolthammer et
15 al.); 6,538,070 (Cardwell, et al.); 6,566,446 (Parikh, et al.); 5,844,045 (Kolthammer et al.); 5,869,575 (Kolthammer et al.); and 6,448,341 (Kolthammer et al.)), 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
20 and propylene-based copolymers (for example, polymers available under the trade designation VERSIFY Plastomers & Elastomers (The Dow Chemical Company) and VISTAMAXX (ExxonMobil Chemical Co.) can also be useful as components in blends comprising the inventive polymer).

Applications

25 The polymers of this invention may be employed in a variety of conventional thermoplastic fabrication processes to produce useful articles, including, but not limited to, monolayer and multilayer films; molded articles, such as blow molded, injection molded, or rotomolded articles; coatings; fibers; and woven or non-woven fabrics.

An inventive polymer may be used in a variety of films, including but not limited to,
30 extrusion coating, food packaging, consumer, industrial, agricultural (applications or films), lamination films, fresh cut produce films, meat films, cheese films, candy films, clarity shrink films, collation shrink films, stretch films, silage films, greenhouse films, fumigation films, liner films, stretch hood, heavy duty shipping sacks, pet food, sandwich bags, sealants, and diaper backsheets.

An inventive polymer is also useful in other direct end-use applications. An inventive polymer may be used for wire and cable coating operations, in sheet extrusion for vacuum forming operations, and forming molded articles, including the use of injection molding, blow molding process, or rotomolding processes.

5 Other suitable applications for the inventive polymers include elastic films and fibers; soft touch goods, such as appliance handles; gaskets and profiles; auto interior parts and profiles; foam goods (both open and closed cell); impact modifiers for other thermoplastic polymers, such as high density polyethylene, or other olefin polymers; cap liners; and flooring.

10

DEFINITIONS

The term "polymer," as used herein, 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 (employed to refer to polymers prepared from only one
15 type of monomer, with the understanding that trace amounts of impurities can be incorporated into the polymer structure), and the term interpolymer as defined hereinafter.

The term "interpolymer," as used herein, refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer includes copolymers (employed to refer to polymers prepared from two different types of
20 monomers), and polymers prepared from more than two different types of monomers.

The term "ethylene-based polymer," as used herein, refers to a polymer that comprises a majority amount of polymerized ethylene monomer (based on weight of the polymer), and, optionally, may contain at least one comonomer.

The term "ethylene/ α -olefin interpolymer," as used herein, refers to an interpolymer
25 that comprises a majority amount of polymerized ethylene monomer (based on the weight of the interpolymer) and at least one α -olefin.

The term, "ethylene/ α -olefin copolymer," as used herein, refers to a copolymer that comprises a majority amount of polymerized ethylene monomer (based on the weight of the copolymer), and an α -olefin, as the only two monomer types.

30 The term "propylene-based polymer," as used herein, refers to a polymer that comprises a majority amount of polymerized propylene monomer (based on weight of the polymer), and, optionally, may comprise at least one comonomer.

The term "composition," as used herein, 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 herein, refers to a mixture of two or more polymers. A blend may or may not be miscible (not phase separated at the molecular level). A blend may or may not be phase separated. A blend may or may not contain one or
5 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).

10 The terms “comprising,” “including,” “having,” and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term “comprising” may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term,
15 “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term “consisting of” excludes any component, step or procedure not specifically delineated or listed.

20 TEST METHODS

Density

Samples for density measurements were prepared according to ASTM D 4703-10. Samples were pressed at 374°F (190°C) for five minutes at 10,000 psi (68 MPa). The temperature was maintained at 374°F (190°C) for the above five minutes, and then the
25 pressure was increased to 30,000 psi (207 MPa) for three minutes. This was followed by a one minute hold at 70°F (21°C) and 30,000 psi (207 MPa). Measurements were made within one hour of sample pressing using ASTM D792-08, Method B.

Melt Index

Melt index, or I2, was measured in accordance with ASTM D 1238-10, Condition
30 190°C/2.16 kg, Method A, and was reported in grams eluted per 10 minutes.

Nuclear Magnetic Resonance (¹³C NMR)

Samples were prepared by adding approximately “3 g of a 50/50 mixture of tetrachloroethane-d2/orthodichlorobenzene, containing 0.025 M Cr(AcAc)₃,” to a “0.25 to 0.40 g polymer sample,” in a 10 mm NMR tube. Oxygen was removed from the sample by

placing the open tubes in a nitrogen environment for at least 45 minutes. The samples were then dissolved and homogenized by heating the tube, and its contents to 150°C, using a heating block and heat gun. Each dissolved sample was visually inspected to ensure homogeneity. Samples were thoroughly mixed, immediately prior to analysis, and were not
5 allowed to cool before insertion into the heated NMR sample holders.

All data were collected using a Bruker 400 MHz spectrometer. The data was acquired using a six second pulse repetition delay, 90-degree flip angles, and inverse gated decoupling, with a sample temperature of 125°C. All measurements were made on non-spinning samples in locked mode. Samples were allowed to thermally equilibrate for seven minutes prior to
10 data acquisition. The ^{13}C NMR chemical shifts were internally referenced to the EEE triad at 30.0 ppm. The C6+ value was a direct measure of C6+ branches in LDPE, where the long branches were not distinguished from chain ends. The 32.2 ppm peak, representing the third carbon from the end of all chains or branches of six or more carbons, was used to determine the C6+ value.

15 **Nuclear Magnetic Resonance (^1H NMR)**

Sample Preparation

The samples were prepared by adding approximately 130 mg of sample to “3.25 g of 50/50, by weight, tetrachlorethane-d2/perchloroethylene” with 0.001 M $\text{Cr}(\text{AcAc})_3$ in a NORELL 1001-7, 10 mm NMR tube. The samples were purged by bubbling N_2 through the
20 solvent, via a pipette inserted into the tube, for approximately five minutes, to prevent oxidation. Each tube was capped, sealed with TEFLON tape, and then soaked at room temperature, overnight, to facilitate sample dissolution. The samples were kept in a N_2 purge box, during storage, before, and after preparation, to minimize exposure to O_2 . The samples were heated and vortexed at 115°C to ensure homogeneity.

25 *Data Acquisition Parameters*

The ^1H NMR was performed on a Bruker AVANCE 400 MHz spectrometer, equipped with a Bruker Dual DUL high-temperature CryoProbe, and a sample temperature of 120°C. Two experiments were run to obtain spectra, a control spectrum to quantitate the total polymer protons, and a double presaturation experiment, which suppressed the intense
30 polymer backbone peaks, and enabled high sensitivity spectra for quantitation of the end-groups. The control was run with ZG pulse, 4 scans, SWH 10,000 Hz, AQ 1.64s, D1 14s. The double presaturation experiment was run with a modified pulse sequence, TD 32768, 100 scans, DS 4, SWH 10,000 Hz, AQ 1.64s, D1 1s, D13 13s.

Data Analysis- ¹H NMR Calculations

The signal from residual ¹H in TCE-d2 (at 6.0 ppm) was integrated, and set to a value of 100, and the integral from 3 to -0.5 ppm was used as the signal from the whole polymer in the control experiment. For the presaturation experiment, the TCE signal was also set to 100,
5 and the corresponding integrals for unsaturation (vinylene at about 5.40 to 5.60 ppm, trisubstituted at about 5.16 to 5.35 ppm, vinyl at about 4.95 to 5.15 ppm, and vinylidene at about 4.70 to 4.90 ppm) were obtained.

In the presaturation experiment spectrum, the regions for cis- and trans-vinylene, trisubstituted, vinyl, and vinylidene were integrated. The integral of the whole polymer from
10 the control experiment was divided by two to obtain a value representing X thousands of carbons (i.e., if the polymer integral = 28,000, this represents 14,000 carbons, and X=14).

The unsaturated group integrals, divided by the corresponding number of protons contributing to that integral, represent the moles of each type of unsaturation per X thousand carbons. Dividing the moles of each type of unsaturation by X, then gives moles unsaturated
15 groups per 1,000 moles of carbons.

Melt Strength

Melt strength measurements were conducted on a Gottfert Rheotens 71.97 (Göettfert Inc.; Rock Hill, SC), attached to a Gottfert Rheotester 2000 capillary rheometer. The melted sample (about 25 to 30 grams) was fed with a Göettfert Rheotester 2000 capillary rheometer,
20 equipped with a flat entrance angle (180 degrees) of length of 30 mm, diameter of 2.0 mm, and an aspect ratio (length/diameter) of 15. After equilibrating the samples at 190°C for 10 minutes, the piston was run at a constant piston speed of 0.265 mm/second. The standard test temperature was 190°C. The sample was drawn uniaxially to a set of accelerating nips, located 100 mm below the die, with an acceleration of 2.4 mm/s². The tensile force was
25 recorded as a function of the take-up speed of the nip rolls. Melt strength was reported as the plateau force (cN) before the strand broke. The following conditions were used in the melt strength measurements: plunger speed = 0.265 mm/second; wheel acceleration = 2.4 mm/s²; capillary diameter = 2.0 mm; capillary length = 30 mm; and barrel diameter = 12 mm.

Dynamic Mechanical Spectroscopy (DMS)

30 Resins were compression-molded into “3 mm thick x 1 inch” circular plaques at 350°F, for five minutes, under 1500 psi pressure, in air. The sample was then taken out of the press, and placed on the counter to cool.

A constant temperature frequency sweep was performed using a TA Instruments “Advanced Rheometric Expansion System (ARES),” equipped with 25 mm (diameter)

parallel plates, under a nitrogen purge. The sample was placed on the plate, and allowed to melt for five minutes at 190°C. The plates were then closed to a gap of 2 mm, the sample trimmed (extra sample that extends beyond the circumference of the “25 mm diameter” plate was removed), and then the test was started. The method had an additional five minute delay
5 built in, to allow for temperature equilibrium. The experiments were performed at 190°C over a frequency range of 0.1 to 100 rad/s. The strain amplitude was constant at 10%. The complex viscosity η^* , $\tan(\delta)$ or $\tan \delta$, viscosity at 0.1 rad/s (V0.1), the viscosity at 100 rad/s (V100), and the viscosity ratio (V0.1/V100) were calculated from these data.

10 **Triple Detector Gel Permeation Chromatography (TDGPC) – Conventional GPC, Light Scattering GPC, Viscometry GPC and gpcBR**

For the GPC techniques used herein (Conventional GPC, Light Scattering GPC, Viscometry GPC and gpcBR), a Triple Detector Gel Permeation Chromatography (3D-GPC or TDGPC) system was used. This system consists of a Robotic Assistant Delivery (RAD) high temperature GPC system [other suitable high temperature GPC instruments include
15 Waters (Milford, Mass) model 150C High Temperature Chromatograph; Polymer Laboratories (Shropshire, UK) Model 210 and Model 220; and Polymer Char GPC-IR (Valencia, Spain)], equipped with a Precision Detectors (Amherst, Mass.) 2-angle laser light scattering (LS) detector Model 2040, an IR4 infra-red detector from Polymer Char (Valencia, Spain), and a 4-capillary solution viscometer (DP) (other suitable viscometers
20 include Viscotek (Houston, Texas) 150R 4-capillary solution viscometer (DP)).

A GPC with these latter two independent detectors and at least one of the former detectors is sometimes referred to as “3D-GPC” or “TDGPC,” while the term “GPC” alone generally refers to conventional GPC. Data collection is performed using Polymer Char GPC-IR software (Valencia, Spain). The system is also equipped with an on-line solvent
25 degassing device from Polymer Laboratories (Shropshire, United Kingdom).

The eluent from the GPC column set flows through each detector arranged in series, in the following order: LS detector, IR4 detector, then DP detector. 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,
30 (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, *Chromatography Polym.*, Chapter 13, (1992)). The triple detector log (MW and intrinsic viscosity) results were optimized using a broad polyethylene standard, as outlined in the section on Light Scattering (LS) GPC below, in the paragraph following Equation (5).

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 13-micron mixed-pore-size packing (Olexis LS, Polymer Labs). Here, the Olexis LS columns were used. The sample carousel compartment was operated at 140°C, and the column
 5 compartment was operated at 150°C. The samples were prepared at a concentration of “0.1 grams of polymer in 50 milliliters of solvent.” The chromatographic solvent and the sample preparation solvent was 1,2,4-trichlorobenzene (TCB) containing 200 ppm of 2,6-di-tert-butyl-4methylphenol (BHT). The solvent was sparged with nitrogen. The polymer samples were gently stirred at 160°C for four hours. The injection volume was 200 microliters. The
 10 flow rate through the GPC was set at 1 ml/minute.

Conventional GPC

For Conventional GPC, the IR4 detector was used, and the GPC column set was calibrated by running 21 narrow molecular weight distribution polystyrene standards. The molecular weight (MW) of the standards ranged from 580 g/mol to 8,400,000 g/mol, and the
 15 standards were contained in six “cocktail” mixtures. Each standard mixture had at least a decade of separation between individual molecular weights. The standard mixtures were purchased from Polymer Laboratories. The polystyrene standards were prepared at “0.025 g in 50 mL of solvent” for molecular weights equal to, or greater than, 1,000,000 g/mol, and at “0.05 g in 50 mL of solvent” for molecular weights less than 1,000,000 g/mol. The
 20 polystyrene standards were dissolved at 80°C, with gentle agitation, for 30 minutes. The narrow standards mixtures were run first, and in order of decreasing “highest molecular weight component” to minimize degradation. The polystyrene standard peak molecular weights were converted to polyethylene molecular weight using Equation (1) (as described in Williams and Ward, J. Polym. Sci., Polym. Letters, 6, 621 (1968)):

$$25 \quad M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B \quad (\text{Eq. 1}),$$

where M is the molecular weight of polyethylene or polystyrene (as marked), and B is equal to 1.0. It is known to those of ordinary skill in the art that A may be in a range of about 0.38 to about 0.44, and is determined at the time of calibration, using a broad polyethylene standard, as outlined in the section on Light Scattering (LS) GPC, below in the paragraph
 30 following Equation (5). Use of this polyethylene calibration method to obtain molecular weight values, such as the molecular weight distribution (MWD or Mw/Mn), and related statistics, is defined here as the modified method of Williams and Ward. The number average molecular weight, the weight average molecular weight, and the z-average molecular

weight are calculated from the following equations.

$$Mw_{cc} = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) M_i = \sum_i w_i M_{cc,i} \quad (\text{Eq. 2});$$

$$M_{n,cc} = \sum w_i / \sum (w_i / M_{cc,i}) \quad (\text{Eq. 3}); \quad M_{z,cc} = \sum (w_i M_{cc,i}^2) / \sum (w_i M_{cc,i}) \quad (\text{Eq. 4}).$$

Light Scattering (LS) GPC

5 For the LS GPC, the Precision Detector PDI2040 detector Model 2040 was used. Depending on the sample, either the 15° angle or the 90° angle of the light scattering detector was used for calculation purposes. Here, the 15° angle was used.

The molecular weight data was obtained in a manner consistent with that published by Zimm (Zimm, B.H., J. Chem. Phys., 16, 1099 (1948)) and Kratochvil (Kratochvil, P.,
10 Classical Light Scattering from Polymer Solutions, Elsevier, Oxford, NY (1987)).

The overall injected concentration used in the determination of the molecular weight was obtained from the mass detector area, and the mass detector constant derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards of known weight average molecular weight. The calculated molecular weights were obtained using a light
15 scattering constant derived from one or more of the polyethylene standards, mentioned below, 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 g/mole. The viscometer calibration can be accomplished using the methods described by the manufacturer, or,
20 alternatively, by using the published values of suitable linear standards, such as Standard Reference Materials (SRM) 1475a (available from National Institute of Standards and Technology (NIST)). The chromatographic concentrations are assumed low enough to eliminate addressing 2nd viral coefficient effects (concentration effects on molecular weight).

With 3D-GPC, absolute weight average molecular weight (“Mw, Abs”) is determined
25 using Equation (5) below, using the “peak area” method for higher accuracy and precision. The “LS Area” and the “Conc. Area” are generated by the chromatograph/detectors combination.

$$M_w = \sum_i w_i M_i = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) M_i = \frac{\sum_i C_i M_i}{\sum_i C_i} = \frac{\sum_i LS_i}{\sum_i C_i} = \frac{LS \text{ Area}}{Conc. \text{ Area}} \quad (\text{Eq. 5})$$

For each LS and viscometry DP profile (for example, see Figures 1, 2, and 3), the x-axis (log MW_{cc}-CPC), where cc refers to the conventional calibration curve, is determined as follows. First, the polystyrene standards (see above) are used to calibrate the retention volume into “log MW_{PS}.” Then, Equation 1 ($M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B$) is used to convert “log MW_{PS}” to “log MW_{PE}.” The “log MW_{PE}” scale serves as the x-axis for the LS profiles of the experimental section (log MW_{PE} is equated to the log MW(cc-CPC)). The y-axis for each LS or DP profile is the LS or DP detector response normalized by the injected sample mass. In Figures 1, 2 and 3, the y-axis for each viscometer DP profile is the DP detector response normalized by the injected sample mass. Initially, the molecular weight and intrinsic viscosity for a linear polyethylene standard sample, such as SRM1475a, or an equivalent, are determined using the conventional calibrations (“cc”) for both molecular weight and intrinsic viscosity as a function of elution volume.

gpcBR Branching Index by Triple Detector GPC (3D-GPC)

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. Upon obtaining the constants, the two values are used to construct two linear reference, conventional calibrations for polyethylene molecular weight and polyethylene intrinsic viscosity as a function of elution volume, as shown in Equations (6) and (7):

$$M_{PE} = \left(\frac{K_{PS}}{K_{PE}} \right)^{1/\alpha_{PE}+1} \cdot M_{PS}^{\alpha_{PS}+1/\alpha_{PE}+1} \quad (\text{Eq. 6}), \quad [\eta]_{PE} = K_{PS} \cdot M_{PS}^{\alpha+1} / M_{PE} \quad (\text{Eq. 7}).$$

The gpcBR branching index is a robust method for the characterization of long chain branching, as described in Yau, Wallace W., “Examples of Using 3D-GPC – TREF for Polyolefin Characterization,” *Macromol. Symp.*, 2007, 257, 29-45. The index avoids 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. From 3D-GPC data, one can obtain the sample bulk absolute weight average molecular weight (M_w, Abs) by the light scattering (LS) detector, using the peak area method. The method avoids the “slice-

by-slice” ratio of light scattering detector signal over the concentration detector signal, as required in a traditional g' determination.

With 3D-GPC, sample intrinsic viscosities are also obtained independently using Equations (8). The area calculation in Equation (5) and (8) offers more precision, because, as
 5 an overall sample area, it is much less sensitive to variation caused by detector noise and 3D-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 Equation (8):

$$IV = [\eta] = \sum_i w_i IV_i = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \frac{\sum_i C_i IV_i}{\sum_i C_i} = \frac{\sum_i DP_i}{\sum_i C_i} = \frac{DP \text{ Area}}{Conc. \text{ Area}} \quad (\text{Eq. 8}),$$

10 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 viscosity detector elution area for the sample polymer is used to determine the intrinsic viscosity (IV or
 15 $[\eta]$) 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 conventional calibrations (“cc”) for both molecular weight and intrinsic viscosity as a function of elution volume, per Equations (2) and (9):

$$[\eta]_{cc} = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \sum_i w_i IV_{cc,i} \quad (\text{Eq. 9}).$$

Equation (10) is used to determine the gpcBR branching index:

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

wherein $[\eta]$ 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
 25 the weight average molecular weight of the conventional calibration. The weight average molecular weight by light scattering (LS) using Equation (5) is commonly referred to as “absolute weight average molecular weight” or “ M_w , Abs.” The $M_{w,cc}$ from Equation (2) using conventional GPC molecular weight calibration curve (“conventional calibration”) is

often referred to as “polymer chain backbone molecular weight,” “conventional weight average molecular weight,” and “ $M_{w,GPC}$.”

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). 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, respectively, for polystyrene.

Once the K and α values have been determined using the procedure discussed previously, the procedure is repeated using the branched samples. The branched samples are analyzed using the final Mark-Houwink constants as the best “cc” calibration values, and Equations (2) – (9) are applied.

The interpretation of gpcBR is straight forward. For linear polymers, gpcBR calculated from Equation (8) 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 long chain branching, because the measured polymer molecular weight 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 value represents the fractional IV change due to the molecular size contraction effect as a 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.

For these particular examples, the advantage of using gpcBR, in comparison to a traditional “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 volume alignment also do not affect the precision of the gpcBR index determination.

Representative Calculation of DP Profile “DPP” – Inventive and Comparative

A GPC elution profile of the concentration-normalized viscometry DP detector response is shown in Figures 1, 2 and 3, for Inventive Example 1, 2 and Comparative Example 1, respectively. The quantities that affect the “DPP” value are defined with the aid

of Figure 1, 2 and 3. The x-axis in the plots is the logarithmic value of the molecular weight (MW) by conventional GPC calculation, or cc-GPC MW. The y-axis is the DP detector response normalized for equal sample concentration, as measured by the peak area of the concentration detector (not shown). The specific features of the DP elution profile are captured in a window defined by two log-MW limits shown in Figures 1, 2 and 3. The lower limit corresponds to a M1 value of 200,000 g/mol, and the upper limit corresponds to a M2 value of 1,355,000 g/mol.

The vertical lines of these two MW limits intersect with the DP elution curve at two points. A line segment is drawn connecting these two intercept points. The height of the DP signal at the first intercept (log M1) gives the DP1 quantity. The height of the DP signal at the second intercept (log M2) gives the DP2 quantity. The steps of calculating the “DPP” quantity are illustrated with three examples (Inventive Example 1, 2 and Comparative Example 3), as shown in Table 1 to 2.

Step 1, calculate “SlopeF” in Table 1, using the following two equations:

$$\text{slope_value} = \frac{DP2 - DP1}{DP2} / d\text{Log}M \tag{Eq. 11}$$

$$\text{DPSF} = \text{a slope function} = \text{Abs}(\text{slope_value}) + 0.01 \tag{Eq. 12}$$

Step 2, calculate “DPP” in Table 2, using the following two equations:

$$\text{DPP} = \text{Log}(\text{DPSF}) + 2 \tag{Eq. 13}$$

Table 1: The “Slope_Value” Calculation

Sample	M1=200,000 g/mol		M2=1,355,000 g/mol		Log(M2)-Log(M1)	
	DP1	Log M1	DP2	Log M2	dLog M	Slope Value
Ex. 1	9.27E-04	5.301	9.11E-04	6.132	0.831	-0.021
Ex. 2	9.24E-04	5.301	8.37E-04	6.132	0.831	-0.12
CE 1	9.01E-04	5.301	6.32E-04	6.132	0.831	-0.513

Table 2: The “DPP” Calculation

Sample	Abs(slope_value)+0.01 DPSF	Log(AreaF+SlopeF)+2 DPP
Ex. 1	0.031	0.4860
Ex. 2	0.134	1.1282
CE 1	0.523	1.7182

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) can be used to measure the melting and crystallization behavior of a polymer over a wide range of temperatures. 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 was melt pressed into a thin film at about 175°C; the melted sample is then air-cooled to room temperature (~25°C). The film sample was formed by pressing a “0.1 to 0.2 gram” sample at 175°C and 1,500 psi, for 30 seconds, to form a “0.1 to 0.2 mil thick” film. A 3-10 mg, “six mm diameter” specimen was extracted from the cooled
5 polymer, weighed, placed in a light aluminum pan (ca 50 mg), and crimped shut. Analysis was then performed to determine its thermal properties.

The thermal behavior of the sample was determined by ramping the sample temperature up and down to create a heat flow versus temperature profile. First, the sample was rapidly heated to 180°C, and held isothermal for five minutes, in order to remove its
10 thermal history. Next, the sample is cooled to -40°C, at a 10 °C/minute cooling rate, and held isothermal at -40°C for five minutes. The sample was then heated to 150°C (this is the “second heat” ramp) at a 10°C/minute heating rate. The cooling and second heating curves were recorded. The cooling curve was analyzed by setting baseline endpoints from the beginning of crystallization to -20°C. The heating curve was analyzed by setting baseline
15 endpoints from -20°C to the end of melt. The values determined were peak melting temperature (T_m), peak crystallization temperature (T_c), heat of fusion (H_f) (in Joules per gram), and the calculated % crystallinity for polyethylene samples using: % Crystallinity = $((H_f)/(292 \text{ J/g})) \times 100$ (Eq. 14).

The heat of fusion and the peak melting temperature were reported from the second
20 heat curve. The peak crystallization temperature was determined from the cooling curve.

Film Testing

The following physical properties were measured on the films as described in the experimental section.

Total (Overall) Haze and Internal Haze: Internal haze and total haze were measured
25 according to ASTM D 1003-07. Internal haze was obtained via refractive index matching using mineral oil (1-2 teaspoons), which was applied as a coating on each surface of the film. A Hazegard Plus (BYK-Gardner USA; Columbia, MD) was used for testing. For each test, five samples were examined, and an average reported. Sample dimensions were “6 in x 6 in.”

30 45° Gloss: ASTM D2457-08 (average of five film samples; each sample “10 in x 10 in”).

Clarity: ASTM D1746-09 (average of five film samples; each sample “10 in x 10 in”).

2% Secant Modulus- MD (machine direction) and CD (cross direction): ASTM D882-10 (average of five film samples in each direction; each sample “1 in x 6 in”).

MD and CD Elmendorf Tear Strength: ASTM D1922-09 (average of 15 film samples in each direction; each sample “3 in x 2.5 in” half moon shape).

5 MD and CD Tensile Strength: ASTM D882-10 (average of five film samples in each direction; each sample “1 in x 6 in”).

Dart Impact Strength: ASTM D1709-09 (minimum of 20 drops to achieve a 50% failure; typically ten “10 in x 36 in” strips).

Puncture Strength: Puncture was measured on an INSTRON Model 4201 with
10 SINTECH TESTWORKS SOFTWARE Version 3.10. The specimen size was “6 in x 6 in,” and four measurements were made to determine an average puncture value. The film was conditioned for 40 hours after film production, and at least 24 hours in an ASTM controlled laboratory (23°C and 50% relative humidity). A “100 lb” load cell was used with a round specimen holder of 4 inch diameter. The puncture probe was a “½ inch diameter” polished
15 stainless steel ball (on a 2.5” rod) with a “7.5 inch maximum travel length.”

There was no gauge length, and the probe was as close as possible to, but not touching, the specimen. The probe was set by raising the probe until it touched the specimen. Then the probe was gradually lowered, until it was not touching the specimen. Then the crosshead was set at zero. Considering the maximum travel distance, the distance would be
20 approximately 0.10 inch. The crosshead speed was 10 inches/minute. The thickness was measured in the middle of the specimen. The thickness of the film, the distance the crosshead traveled, and the peak load were used to determine the puncture by the software. The puncture probe was cleaned using a “KIM-WIPE” after each specimen.

Shrink Tension: Shrink tension was measured according to the method described in
25 Y. Jin, T. Hermel-Davidock, T. Karjala, M. Demirors, J. Wang, E. Leyva, and D. Allen, “Shrink Force Measurement of Low Shrink Force Films”, SPE ANTEC Proceedings, p. 1264 (2008). The shrink tension of film samples was measured through a temperature ramp test that was conducted on an RSA-III Dynamic Mechanical Analyzer (TA Instruments; New Castle, DE) with a film fixture. Film specimens of “12.7 mm wide” and “63.5 mm long”
30 were die cut from the film sample, either in the machine direction (MD) or the cross direction (CD), for testing. The film thickness was measured by a Mitutoyo Absolute digimatic indicator (Model C112CEXB). This indicator had a maximum measurement range of 12.7 mm, with a resolution of 0.001 mm. The average of three thickness measurements, at different locations on each film specimen, and the width of the specimen, were used to

calculate the film's cross sectional area (A), in which "A = Width × Thickness" of the film specimen that was used in shrink film testing. A standard film tension fixture from TA Instruments was used for the measurement. The oven of the RSA-III was equilibrated at 25°C, for at least 30 minutes, prior to zeroing the gap and the axial force. The initial gap was set to 20 mm. The film specimen was then attached onto both the upper and the lower fixtures. Typically, measurements for MD only require one ply film. Because the shrink tension in the CD direction is typically low, two or four plies of films are stacked together for each measurement to improve the signal-to-noise ratio. In such a case, the film thickness is the sum of all of the plies. In this work, a single ply was used in the MD direction and two plies were used in the CD direction. After the film reached the initial temperature of 25°C, the upper fixture was manually raised or lowered slightly to obtain an axial force of -1.0 g. This was to ensure that no buckling or excessive stretching of the film occurred at the beginning of the test. Then the test was started. A constant fixture gap was maintained during the entire measurement.

The temperature ramp started at a rate of 90°C/min, from 25°C to 80°C, followed by a rate of 20°C/min, from 80°C to 160°C. During the ramp from 80°C to 160°C, as the film shrunk, the shrink force, measured by the force transducer, was recorded as a function of temperature for further analysis. The difference between the "peak force" and the "baseline value before the onset of the shrink force peak" is considered the shrink force (F) of the film. The shrink tension of the film is the ratio of the shrink force (F) to the initial cross sectional area (A) of the film.

EXPERIMENTAL

Preparation of Inventive Ethylene-Based Polymers

Figure 4 is a block diagram of the process reaction system used to produce the examples. The process reaction system in Figure 4 is a partially closed-loop, dual recycle high-pressure, low density polyethylene production system. The process reaction system is comprised of a fresh ethylene feed line 1; a booster/primary compressor "BP", a hypercompressor "Hyper," a three zone adiabatic autoclave reactor, coupled with a short tube reactor. The autoclave reactor consists of split ethylene feed 50/50 which is fed to the top of the reactor (top ethylene feed), zone 1, and to the side of the reactor (bottom ethylene feed) at zone 2. A first peroxide initiator, line 2, is injected into the first zone; a second peroxide initiator, line 3, is injected into the ethylene stream, just before entering the second zone (bottom ethylene feed); a third peroxide initiator, line 4, is injected into the third zone of

the autoclave. Finally a fourth peroxide initiator, line 5, is connected to the inlet of the short tube reactor; the short tube reactor uses cooling jackets (using high pressure water), which are mounted around the outer shell of the short tube reactor. The polymer and ethylene are then separated using a high pressure separator "HPS"; a high pressure recycle, line 6; a low pressure separator "LPS"; a low pressure recycle line 7. A chain transfer agent, line 8, is then injected into the suction side of the booster/primary. Although the process is capable of running all three reaction zones in the autoclave portion of the reactor, zone 3 was not utilized.

For the Inventive Examples 1-3 and Comparative Example 1, a mixture containing t-butyl peroxy-2 ethylhexanoate (TBPO), t-butyl peroxyacetate (TPA), and an iso-paraffinic hydrocarbon solvent (boiling range $>179^{\circ}\text{C}$) are used as the initiator mixture for the first and second injection points. For the short tube initiator injection point, a mixture containing di-t-butyl peroxide (DTBP), TPA, TPBO, and the iso-paraffinic hydrocarbon solvent are used. Table 3 shows the composition in wt% of the peroxide initiator and solvent solution used for each of the injection points.

Isobutane was used as the chain transfer agent. The isobutane is injected into the ethylene stream at the suction side of the booster/primary compressor (BP). The composition of the CTA feed to the process is adjusted to maintain the melt index of the product. The process conditions are given in Table 4. The reaction temperatures for each autoclave zone and to the short tube are controlled by adjusting peroxide flows to each of the reaction zones. The reactor pressure and the reactor control temperatures are used to ultimately control the molecular weight distribution of the product. The total fresh isobutane flow is lower for the Inventive Examples when compared to the Comparative Example. The lower flow rates are needed to reduce the total amount of CTA going to the reactor. The lower CTA concentration, in combination with the other disclosed process conditions, results in resins with the inventive properties described herein.

Properties of inventive LDPEs and comparative LDPEs (including some commercial LDPEs) are listed in Tables 5-10. Table 5 contains the melt index (I2), density, melt strength, and the velocity at break of the melt strength data. The inventive materials in particular exhibit a relatively low melt index with high melt strength, along with a relatively high velocity at break, considering the low melt index. This in particular is important when the Inventive Examples are used in film applications, in which drawability, bubble stability, output, and processability are important. If the melt strength is increased, in some cases, above that of the inventive examples, the velocity at break will drop; the drawdown, for

example in an extrusion coating line, will drop; the material may not blend as well with other materials, such as LLDPE; and the propensity to form gels in the blend or film may be greater, making the LDPE undesirable for use in some film or other applications.

5 Table 6 contains the TDGPC data, illustrating for the inventive examples the relatively broad molecular weight distribution or MWD(conv) [(Mw(conv)/Mn(conv))], and relatively high cc-GPC Mw and cc-GPC Mz. Table 6 also contains the TDGPC-related properties derived from the LS and viscosity detectors, in conjunction with the concentration detector showing that the inventive examples have a relatively high Mw-abs, Mw(LS-abs)/Mw(cc-GPC), IVw, gpcBR, IVcc, IVcc/IVw, and low DPP, which are a reflection of the
10 relatively broad molecular weight distribution, coupled with relatively high long chain branching. This design is optimized to give the best balance of overall melt index and melt strength, in order to give a good balance of physical properties, along with good drawability, bubble stability, output, and processability, when forming films or coatings with this LDPE or blends with this LDPE.

15 Table 7 contains the DMS viscosity data, as summarized by the viscosities measured at 0.1, 1, 10, and 100 rad/s, the viscosity ratio or the ratio of viscosities measured at 0.1 rad/s to that measured at 100 rad/s, all being measured at 190°C, and the tan delta measured at 0.1 rad/s. The low frequency viscosity, the viscosity at 0.1 rad/s, is relatively high for the Inventive Examples as compared to the Comparative Examples. A high “low frequency
20 viscosity” may be correlated with good melt strength, bubble stability, and film output. The viscosity ratio, which reflects the change in viscosity with frequency, is of “intermediate to low” value for the Inventive Examples as compared to the Comparative Examples.

Table 8 contains the branches per 1000C as measured by ¹³C NMR. These LDPE polymers contain amyl, or C5 branches, which are not contained in substantially linear
25 polyethylenes, such as AFFINITY Polyolefin Plastomers, or Ziegler-Natta catalyzed LLDPE, such as DOWLEX, both produced by The Dow Chemical Company. Each inventive and comparative LDPE contained greater than, or equal to, 0.5 amyl groups (branches) per 1000 carbon atoms (the inventive examples contain greater than 2.0 amyl groups (branches) per 1000 carbon atoms).

30 Table 9 contains unsaturation results by ¹H NMR. Table 10 contains the DSC results of the melting point, T_m, the heat of fusion, the percent crystallinity, and the crystallization point, T_c.

Table 3: Peroxide initiator compositions in wt% at each injection point used.

Injection Point	Material	Ex. 1 wt%	Ex. 2 wt%	CE 1 wt%	Ex. 3 wt%
#1	TBPO	10	10	10	10
#1	TPA	10	10	10	10
#1	Solvent	80	80	80	80
#2	TBPO	10	10	10	10
#2	TPA	10	10	10	10
#2	Solvent	80	80	80	80
#3	TBPO	0	0	0	0
#3	TPA	0	0	0	0
#3	Solvent	0	0	0	0
#4	TBPO	6.3	6.3	6.3	6.3
#4	TPA	3.5	3.5	3.5	3.5
#4	DTBP	4.2	4.2	4.2	4.2
#4	Solvent	86	86	86	86

Table 4: Process conditions used to manufacture the Examples (T is used as an abbreviation for temperature, N/A for not applicable, and BW for boiling water).

	Ex. 1	Ex. 2	CE 1	Ex. 3
Reactor Pressure (Psig)	21,500	21,500	21,500	21,500
Top Feed T (°C)	74	74	74	72
Bottom Feed T (°C)	32	32	32	34
Zone 1 T (°C)	246	246	245	245
Zone 2 T (°C)	245	245	245	245
Re-initiation T (°C)	207	208	209	212
Short Tube Peak T (°C)	285	285	285	286
Fresh Ethylene Flow (lb/hr)	18,115	18,400	18,310	19,595
Ethylene Throughput to Reactor (lb/hr)	78,000	78,000	78,000	78,000
Ethylene Conversion (%)	19.2	19.5	19.4	20.7
Isobutane Flow (lb/hr)	14.5	25	40	13.5
Ethylene Purge Flow (lb/hr)	2,296	2,100	2,100	2,230
BW Drum T to Short Tube (°C)	304	304	304	304
BW Return T from Short Tube (°C)	318	318	318	317

5

Table 5: Melt Index (I2), Density, Melt Strength (MS) and Velocity at Break at 190°C of Examples and Comparative Examples.

Sample	I2 (190 °C)	Density (g/cc)	Melt strength (cN)	Melt Strength Velocity at Break (mm/s)
Ex. 1	0.60	0.9178	25.5	85
Ex. 2	0.75	0.9178	24.8	142
CE 1	1.42	0.9182	19.5	184
CE 2	0.17	0.9184	19.5	54
CE 3	0.38	0.9182	30.0	72
CE 4	0.64	0.9205	12.1	162
CE 5	0.44	0.9244	11.5	172
CE 6	0.37	0.9276	12.6	116
CE 7	0.24	0.9215	15.1	53
CE 8	0.49	0.9274	11.8	91
CE 9	0.63	0.9262	11.6	133
CE 10	0.70	0.9269	11.6	153
CE 11	0.23	0.9189	21.8	54
CE 12	0.26	0.9179	25.8	47
CE 13	0.26	0.9251	18.6	74
CE 14	0.85	0.9240	13.1	237
CE 15	0.17	0.9225	16.6	62
CE 16	0.61	0.9269	13.4	124
CE 17	1.08	0.9240	10.2	335
CE 18	0.82	0.9230	16.5	273
CE 19	0.25	0.9200	17.4	78
CE 20	0.90	0.9328	6.5	274
CE 21	0.15	0.9200	19.4	53
CE 22	0.39	0.9190	16.2	74
CE 23	0.28	0.9278	15.6	70
CE 24	0.73	0.9236	16.2	183
CE 25	0.70	0.9235	10.8	132
Ex. 3	0.61	0.9176	23.3	93
CE 26	2.12	0.9178	16.5	229

Table 6: TDGPC-related properties (conventional calibration) of Examples and Comparative Examples, and TDGPC-related properties (derived from LS and viscosity detectors in conjunction with the concentration detector).

Sample	cc-GPC Mn (g/mol)	cc-GPC Mw (g/mol)	cc-GPC Mz (g/mol)	cc-GPC Mw/Mn	Mw-abs (g/mol)	Mw(LS-abs) / Mw(cc-GPC)	IVw (dl/g)	gpcBR	IVcc (dl/g)	IVcc/IVw	DPP = 2 + LOG(SF)
Ex. 1	19,987	212,146	755,540	10.61	657,714	3.10	1.18	3.90	2.66	2.26	0.49
Ex. 2	19,549	206,114	747,153	10.54	635,154	3.08	1.16	3.85	2.60	2.25	1.13
CE 1	18,959	180,371	669,267	9.51	527,598	2.93	1.09	3.54	2.36	2.17	1.72
CE 2	19,992	143,606	459,058	7.18	336,652	2.34	1.19	2.30	2.08	1.75	2.75
CE 3	24,050	255,596	901,799	10.63	951,706	3.72	1.27	5.27	3.04	2.38	1.42
CE 4	15,463	101,916	330,862	6.59	211,371	2.07	1.00	1.79	1.63	1.63	3.21
CE 5	20,044	87,096	262,188	4.35	164,284	1.89	1.01	1.36	1.49	1.48	3.48
CE 6	20,432	90,529	261,099	4.43	184,461	2.04	1.02	1.57	1.54	1.50	3.44
CE 7	18,327	108,779	344,274	5.94	225,070	2.07	1.08	1.73	1.72	1.59	3.20
CE 8	20,111	102,166	345,225	5.08	180,442	1.77	1.06	1.35	1.63	1.54	3.04
CE 9	18,194	98,424	340,388	5.41	181,596	1.85	1.02	1.44	1.58	1.55	3.10
CE 10	18,703	100,434	350,396	5.37	190,569	1.90	1.03	1.48	1.60	1.56	3.05
CE 11	19,504	129,761	405,912	6.65	290,561	2.24	1.14	2.10	1.94	1.71	2.99
CE 12	18,406	141,179	451,348	7.67	316,844	2.24	1.15	2.22	2.05	1.78	2.80
CE 13	22,343	106,907	267,377	4.78	184,786	1.73	1.10	1.39	1.74	1.59	3.79
CE 14	17,895	93,157	293,489	5.21	195,785	2.10	0.98	1.72	1.55	1.58	3.31
CE 15	19,379	114,951	385,618	5.93	257,569	2.24	1.11	1.90	1.78	1.60	3.01
CE 16	17,287	101,768	333,400	5.89	182,589	1.79	1.02	1.46	1.63	1.61	3.20
CE 17	20,412	84,867	192,476	4.16	124,474	1.47	0.96	1.07	1.49	1.55	4.68
CE 18	20,224	98,856	253,926	4.89	154,163	1.56	1.00	1.29	1.64	1.63	4.09
CE 19	17,199	114,533	376,996	6.66	266,655	2.33	1.07	2.11	1.77	1.66	3.08
CE 20	24,463	65,652	135,683	2.68	97,247	1.48	0.97	0.72	1.27	1.31	4.03
CE 21	17,160	125,170	319,287	7.29	278,963	2.23	1.18	1.96	1.93	1.64	3.78
CE 22	12,727	118,433	375,099	9.31	275,647	2.33	1.08	2.20	1.81	1.68	3.10
CE 23	18,431	109,716	354,514	5.95	208,452	1.90	1.08	1.55	1.72	1.60	3.11
CE 24	22,545	105,649	274,411	4.69	199,066	1.88	1.04	1.65	1.72	1.66	3.73
CE 25	18,535	86,468	280,330	4.67	148,996	1.72	1.00	1.18	1.46	1.46	3.39
Ex. 3	19,768	212,222	744,756	10.74	689,842	3.25	1.17	4.34	2.66	2.27	0.87

Table 7: Viscosities in Pa•s at 0.1, 1, 10, and 100 rad/s, the viscosity ratio, and the tan delta at 190°C.

Sample	Visc 0.1 rad/s (Pa•s)	Visc 1 rad/s (Pa•s)	Visc 10 rad/s (Pa•s)	Visc 100 rad/s (Pa•s)	Vis. Ratio	Tan Delta 0.1 rad/s
Ex. 1	17,296	6,940	2,178	578	29.9	1.7
Ex. 2	15,293	6,355	2,047	554	27.6	1.8
CE 1	9,475	4,502	1,591	461	20.5	2.3
CE 2	44,635	14,203	3,672	816	54.7	1.2
CE 3	21,127	8,089	2,470	639	33.0	1.6
CE 4	20,309	8,480	2,566	635	32.0	2.0
CE 5	27,013	11,419	3,492	858	31.5	2.0
CE 6	28,266	12,057	3,723	913	31.0	2.1
CE 7	40,705	14,261	3,849	863	47.2	1.5
CE 8	24,204	10,186	3,178	811	29.8	2.0
CE 9	19,811	8,715	2,835	736	26.9	2.1
CE 10	19,105	8,424	2,742	713	26.8	2.1
CE 11	40,473	13,554	3,600	823	49.2	1.3
CE 12	37,944	12,276	3,206	730	52.0	1.3
CE 13	37,164	14,111	4,034	939	39.6	1.7
CE 14	16,593	7,709	2,542	663	25.0	2.4
CE 15	47,127	15,488	4,024	881	53.5	1.3
CE 16	22,066	9,470	2,985	751	29.4	2.1
CE 17	11,627	6,437	2,377	666	17.5	3.8
CE 18	17,063	7,810	2,546	667	25.6	2.3
CE 19	34,788	12,138	3,289	758	45.9	1.4
CE 20	10,755	6,638	2,652	786	13.7	4.8
CE 21	53,524	17,221	4,406	953	56.2	1.3
CE 22	28,178	10,815	3,125	741	38.0	1.7
CE 23	36,174	13,602	3,899	914	39.6	1.6
CE 24	16,153	8,048	2,803	751	21.5	2.9
CE 25	19,388	8,702	2,860	749	25.9	0.7
Ex. 3	18,414	7,257	2,269	596	30.9	1.6
CE 26	6,250	3,236	1,244	384	16.3	2.9

Table 8: Branching results in branches per 1000C by ¹³C NMR of Examples and Comparative Examples.

Sample	1,3 diethyl branches	C2 on Quat Carbon	C4	C5	C6+
Ex. 1	4.6	2.0	7.3	2.2	3.1
Ex. 2	4.8	1.9	7.4	2.2	3.2
CE 3	4.7	1.9	7.3	2.6	3.6
Ex. 3	4.7	1.9	7.4	2.3	3.2
CE 27***	ND	ND	ND	ND	19.5*
CE 28****	ND	ND	ND	ND	11.4*

* The values in the C6+ column for the DOWLEX and AFFINITY samples represent C6 branches from octene only, and do not include chain ends.

5 **ND = not detected.

***AFFINITY PL 1880

****DOWLEX 2045G

Table 9: Unsaturation results by ¹H NMR of Examples and Comparative Examples.

Sample	vinyl/1000C	cis and trans / 1000C	trisub / 1000C	vinylidene / 1000C	total unsaturation / 1000C
Ex. 1	0.037	0.032	0.032	0.226	0.38
Ex. 2	0.038	0.033	0.033	0.225	0.38
CE 3	0.039	0.036	0.036	0.232	0.39
Ex. 3	0.045	0.038	0.102	0.235	0.42
CE 27***	0.040	0.064	0.123	0.043	0.27
CE 28****	0.283	0.049	0.042	0.055	0.43

10

***AFFINITY PL 1880

****DOWLEX 2045G

Table 10: DSC results of Examples and Comparative Examples.

Sample	T _m (°C)	Heat of Fusion (J/g)	% Crystallinity	T _c (°C)
Ex. 1	107.6	135.6	46.4	95.3
Ex. 2	107.6	136.4	46.7	95.3
CE 3	107.3	136.2	46.6	95.6
Ex. 3	107.6	141.1	48.3	95.3

15 Formulations

Blown films were made, and physical properties measured, with different LDPEs and one LLDPE, LLDPE1 (DOWLEX 2045G). LLDPE1 had a “1.0 melt index (MI or I2), and a

0.920 g/cc density.” Films were made at 20 wt% and 80 wt% of the respective LDPE, based on the weight of the LDPE and LLDPE1.

Each formulation was compounded on a MAGUIRE gravimetric blender. A polymer processing aid (PPA), DYNAMAR FX-5920A, was added to each formulation. The PPA
5 was added at “1.125 wt% of masterbatch,” based on the total weight of the weight of the formulation. The PPA masterbatch (Ingenia AC-01-01, available from Ingenia Polymers) contained 8 wt% of DYNAMAR FX-5920A in a polyethylene carrier. This amounts to 900 ppm PPA in the polymer.

LLDPE1 was also used as the LLDPE in the films made at maximum output. All of
10 these samples were made with 80 wt% DOWLEX 2045G and 20 wt% LDPE.

Production of Blown Films

The monolayer blown films were made on an “8 inch die” with a polyethylene “Davis Standard Barrier II screw.” External cooling by an air ring and internal bubble cooling were used. General blown film parameters used to produce each blown film are shown in Table
15 11. The temperatures are the temperatures closest to the pellet hopper (Barrel 1), and in increasing order, as the polymer was extruded through the die.

Table 11: Blown film fabrication conditions for films.

% LDPE	0 and 20	80
Blow up ratio (BUR)	2.5	2.5
Output (lb/hr), Standard Rate	250	250
Film thickness	2.0	2.0
Die gap (mil)	70	70
Air temperature (°F)	45	45
Temperature profile (°F)		
Barrel 1	350	350
Barrel 2	425	445
Barrel 3	380	365
Barrel 4	325	400
Barrel 5	325	345
Screen Temperature	430	345
Adapter	430	440
Block	430	440
Lower Die	440	440
Inner Die	440	440
Upper Die	440	440

Production of Films for Determination of Maximum Output Rate of Blown Film

Film samples were made at a controlled rate and at a maximum rate. The controlled rate was 250 lb/hr, which equals an output rate of 10.0 lb/hr/inch of die circumference. The die diameter used for the maximum output trials was an 8 inch die, so that for the controlled rate, as an example, the conversion between “lb/hr” and “lb/hr/inch” of die circumference, is shown in Equation 15. Similarly, such an equation can be used for other rates, such as the maximum rate, by substituting the maximum rate in Equation 15 to determine the “lb/hr/inch” of die circumference.

$$\text{Lb/Hr/Inch of Die Circumference} = (250 \text{ Lb/Hr}) / (8 * \pi) = 10 \quad (\text{Eq. 15})$$

The maximum rate for a given sample was determined by increasing the output rate to the point where bubble stability was the limiting factor. The extruder profile was maintained for both samples (standard rate and maximum rate), however the melt temperature was higher for the maximum rate samples, due to the increased shear rate with higher motor speed (rpm, revolutions per minute). The maximum bubble stability was determined by taking the bubble to the point where it would not stay seated in the air ring. At that point, the rate was reduced to where the bubble was reseated in the air ring, and then a sample was collected. The cooling on the bubble was adjusted by adjusting the air ring and maintaining the bubble. This was taken as the maximum output rate while maintaining bubble stability.

Film properties are listed in Tables 12-14. As seen in Table 12, it has been discovered that the Inventive Examples have excellent optics of haze, gloss, and clarity compared to the highest melt strength LDPE, CE3, blend (Film #1) and 100% LLDPE (Film #7) at standard rates. All Inventive Example blend films have similar toughness in terms of tear (MD) and dart compared to the Comparative Example blends, which is important as it is desired to maintain toughness, while enhancing output.

As seen in Table 13, it has been discovered that the Inventive Examples Ex. 1 and Ex. 2 have significantly improved maximum output over LDPE, CE7, blend (Film # 12); LDPE, CE26, blend (Film #13); and 100% LLDPE (Film #14). All Inventive Examples have excellent optics of haze, gloss, and clarity, compared to the highest melt strength LDPE, CE3, blend (Film #8) and 100% LLDPE (Film #14) at maximum rates. All Inventive Example LDPE blend films have similar toughness in terms of tear (MD), dart, and puncture compared to the highest melt strength LDPE, CE3, blend (Film #8) which is important as it is desired to maintain toughness, while enhancing output.

As seen in Table 14, it has been discovered that the Inventive Examples have excellent optics of haze, gloss, and clarity compared to the highest melt strength LDPE, CE3, blend (Film #15) at standard rates. All Inventive Example blend films have similar or improved toughness in terms of tear (MD), dart, and puncture, compared to the highest melt strength LDPE, CE3, blend (Film #15) at standard rates, which is important, as it is desired to
5 maintain toughness while enhancing output.

Table 12: Film properties of 80% LLDPE1/20% LDPE and 100% LLDPE1 Films #1 – 7 made at 2 mil at a standard rate of 250 lb/hr (8" die).

Film #	1	2	3	4	5	6	7
Component 1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1
Wt% Component 1	80	80	80	80	80	80	100
Component 2	CE 3	Ex. 1	Ex. 2	CE 1	CE 7	CE 26	NA
Wt% Component 2	20	20	20	20	20	20	NA
Haze (%)	15.9	11.7	10.5	8.9	7.7	8.7	17.0
Haze, Internal (%)	3.0	3.2	3.1	3.7	2.9	3.8	5.2
45 Degree Gloss (%)	42.9	53.7	58.1	65.4	67.8	68.1	42.7
Clarity (%)	81.7	89.5	92.1	95.3	97.2	96.2	97.6
MD Tear, Elmendorf Type B (g)	449	422	413	443	469	453	885
CD Tear, Elmendorf Type B (g)	1,271	1,159	1,312	1,245	1,547	1,296	1,095
Normalized MD Tear (g/mil)	211	201	199	213	217	223	424
Normalized CD Tear (g/mil)	598	550	629	598	709	622	519
Dart A (g)	262	244	274	268	283	268	463
Puncture (ft-lb _f /in ³)	214	223	212	226	251	212	302
2% MD Secant Modulus (psi)	27,209	27,332	26,151	28,647	28,258	27,750	26,515
2% CD Secant Modulus (psi)	34,168	33,724	32,705	34,487	31,981	34,003	30,823
MD Shrink Tension (psi)	11.82	13.21	11.21	9.64	12.08	8.94	2.99
CD Shrink Tension (psi)	0.49	0.57	0.57	0.58	0.51	0.63	0.58
Thickness (mil)	2.12	2.1	1.98	2.05	2.08	2.08	2.08
Frost Line Height (inches)	32	32	32	32	32	32	32
Melt Temperature (°F)	427	424	423	422	427	421	431

Table 13: Film properties of 80% LLDPE1/20% LDPE and 100% LLDPE1 Films #8 – 14 made at 2 mil at a maximum rate (8" die).

Film #	8	9	10	11	12	13	14
Component 1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1
Wt% Component 1	80	80	80	80	80	80	100
Component 2	CE 3	Ex. 1	Ex. 2	CE 1	CE 7	CE 26	NA
Wt% Component 2	20	20	20	20	20	20	NA
Haze (%)	14.4	10.7	10.4	9.5	8.4	9.7	21.0
Haze, Internal (%)	3.6	3.7	3.6	4.1	3.6	4.4	5.4
45 Degree Gloss (%)	46.6	59.5	59.9	65.5	66.4	66.1	35.3
Clarity (%)	85.6	92.5	92.7	95.3	95.9	95.7	95.8
MD Tear (g)	428	461	416	428	369	514	909
CD Tear (g)	1,427	1,389	1,449	1,275	1,517	1,260	1,065
Normalized MD Tear (g/mil)	201	220	194	205	173	243	429
Normalized CD Tear (g/mil)	635	649	677	610	701	588	496
Dart A (g)	232	256	253	256	247	256	439
Puncture (ft-lb/in ³)	199	230	216	204	222	230	311
2% MD Secant Modulus (psi)	27,176	28,549	27,531	28,661	28,450	27,086	26,431
2% CD Secant Modulus (psi)	34,710	34,997	32,682	34,449	30,765	33,513	33,035
MD Shrink Tension (psi)	13.17	11.62	10.91	10.50	13.75	7.76	3.01
CD Shrink Tension (psi)	0.62	0.46	0.47	0.64	0.33	0.52	0.39
Thickness (mil)	2.24	2.11	2.1	2.09	2.09	2.1	2.06
Frost Line Height (inches)	70	69	67	60	70	59	57
Melt Temperature (°F)	466	459	456	447	457	447	447
Maximum rate output (lb/hr)	504	484	476	434	467	443	345
Maximum rate output (lb/hr/in)	20.1	19.3	18.9	17.3	18.6	17.6	13.7

Table 14: Film Properties of 20% LLDPE/80% LDPE and 100% LLDPE1 Films # 15-20 made at 2 mil at a standard rate of 250 lb/hr (8" die).

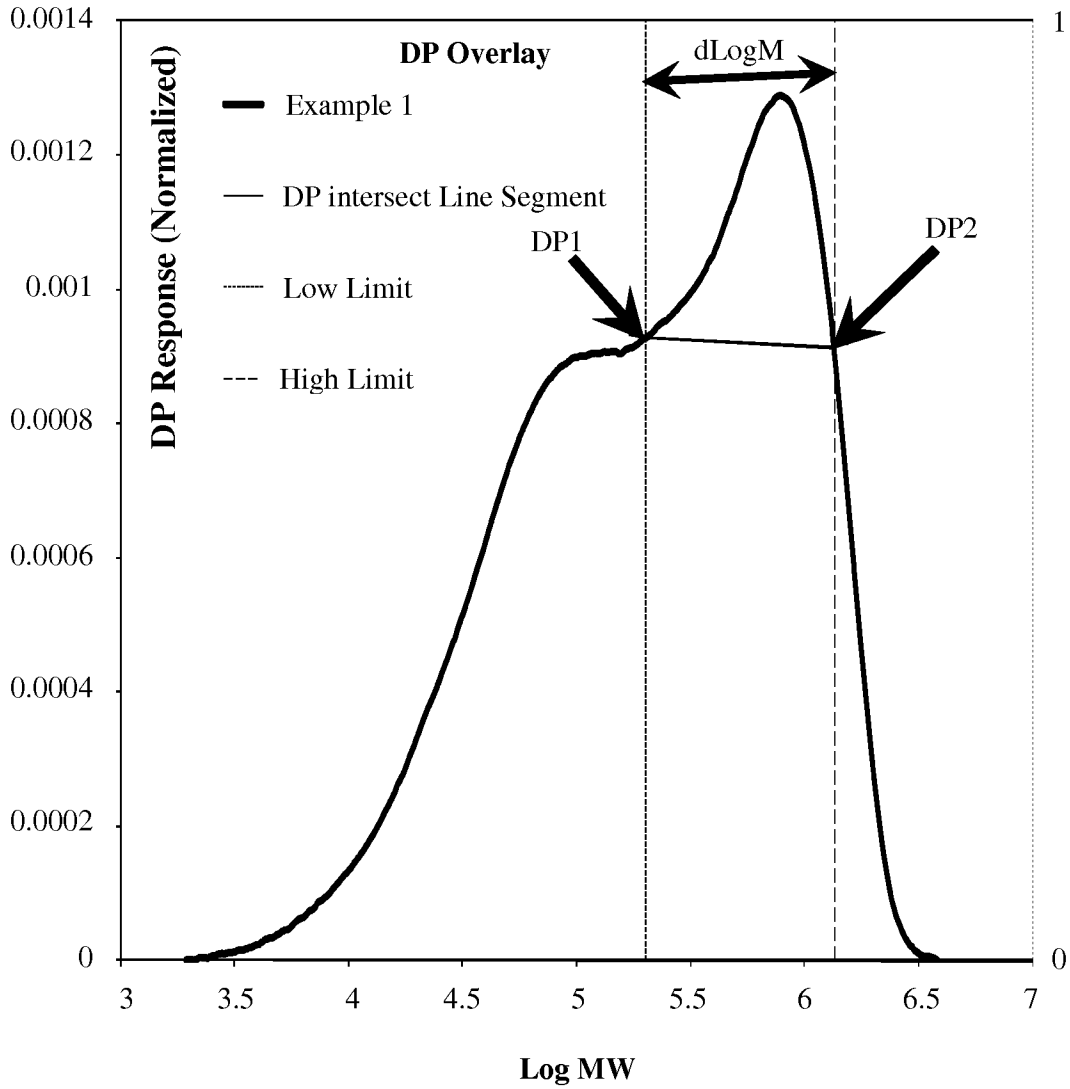
Film #	15	16	17	18	19	20
Component 1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1	LLDPE1
Wt% Component 1	20	20	20	20	20	20
Component 2	CE 3	Ex. 1	Ex. 2	CE 1	CE 7	CE 26
Wt% Component 2	80	80	80	80	80	80
Haze (%)	36.40	25.56	22.42	16.96	10.44	14.98
Haze, Internal (%)	1.48	2.49	1.75	2.39	1.42	3.04
45 Degree Gloss (%)	17.40	25.20	28.40	37.20	52.20	43.32
Clarity (%)	48.78	63.84	67.35	74.86	89.48	80.58
MD Tear (g)	105	130	129	185	232	218
CD Tear (g)	297	322	334	329	348	354
Normalized MD Tear (g/mil)	54	64	63	85	111	102
Normalized CD Tear (g/mil)	152	156	164	153	166	168
Dart A (g)	139	163	160	130	136	103
Puncture (ft-lb/in ³)	68	75	78	61	90	57
2% MD Secant Modulus (psi)	30,149	28,775	27,696	26,337	32,082	24,784
2% CD Secant Modulus (psi)	34,062	33,321	32,296	31,043	38,086	29,890
MD Shrink Tension (psi)	45.11	30.17	36.18	26.04	35.97	19.46
CD Shrink Tension (psi)	0.33	0.14	0.20	0.37	0.65	0.29
Thickness (mil)	1.92	2.03	1.99	2.12	2.06	2.07

CLAIMS

1. A composition comprising an ethylene-based polymer, which is a low density polyethylene (LDPE) obtained by free radical polymerization of ethylene, and wherein the LDPE has a GPC-Viscometer parameter "DPP" less than 1.3.
- 5
2. The composition of claim 1, wherein the polymer has a MWD(conv) from 8 to 13.
3. The composition of claim 1 or claim 2, wherein the polymer has a melt strength greater than 20 cN.
- 10
4. The composition of any of the previous claims, wherein the polymer has a gpcBR value from 2.0 to 5.0.
5. A composition comprising an ethylene-based polymer that comprises the following
- 15 features:
- a) at least 0.1 amyl groups per 1000 total carbon atoms;
 - b) a melt index from 0.5 to 0.9
 - c) a MWD(conv) [(Mw(conv)/Mn(conv))] from 9 to 13.
- 20
6. A composition comprising an ethylene-based polymer that comprises the following features:
- a) at least 0.1 amyl groups per 1000 total carbon atoms;
 - b) a MWD(conv) from 9 to 13;
 - c) a gpcBR value from 2.0 to 5.0;
 - d) a melt strength (MS) greater than 20 cN.
- 25
7. The composition of claim 5 or claim 6, wherein the ethylene-based polymer has a GPC-Viscometer parameter "DPP" less than 2.0.
- 30
8. The composition of any of the previous claims, wherein the polymer has a melt index (I2) from 0.01 to 1 g/10 min.

9. The composition of any of the previous claims, wherein the polymer has a density from 0.910 to 0.940 g/cc.
10. The composition of any of the previous claims, wherein the polymer has a melt
5 strength of at least 22 cN and less than 27 cN.
11. The composition of any of the previous claims, wherein the polymer has a viscosity ratio ($V_{0.1} / V_{100}$, at 190°C) from 25 to 35.
- 10 12. The composition of any of the previous claims, wherein the polymer has a MWD(conv) greater than 9.5.
13. The composition of any of the previous claims, wherein the ethylene-based polymer is a low density polyethylene (LDPE) formed by a high pressure, free radical polymerization of
15 ethylene.
14. An article comprising at least one component formed from the composition of any of the previous claims.
- 20 15. The article of claim 13, wherein the article is a film.

FIGURE 1



5

DPP Calculation

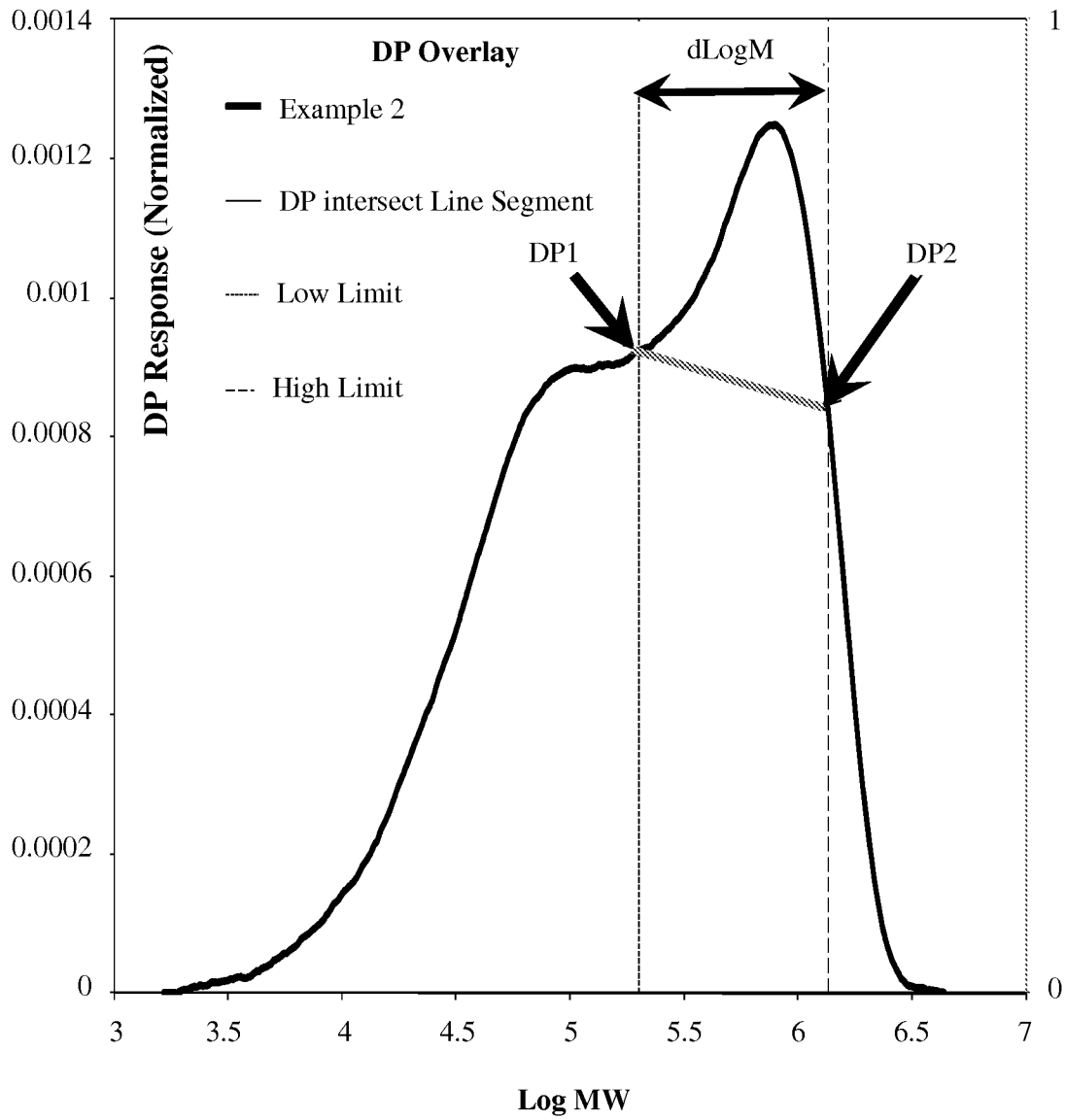
Low MW = 200,000
 High MW = 1,355,000

$Slope = (DP2 - DP1) / DP2 / dLogM$
 $DPSF = abs(Slope) + 0.001$

$DPP = Log(DPSF) + 2$

10

FIGURE 2



5

DPP Calculation

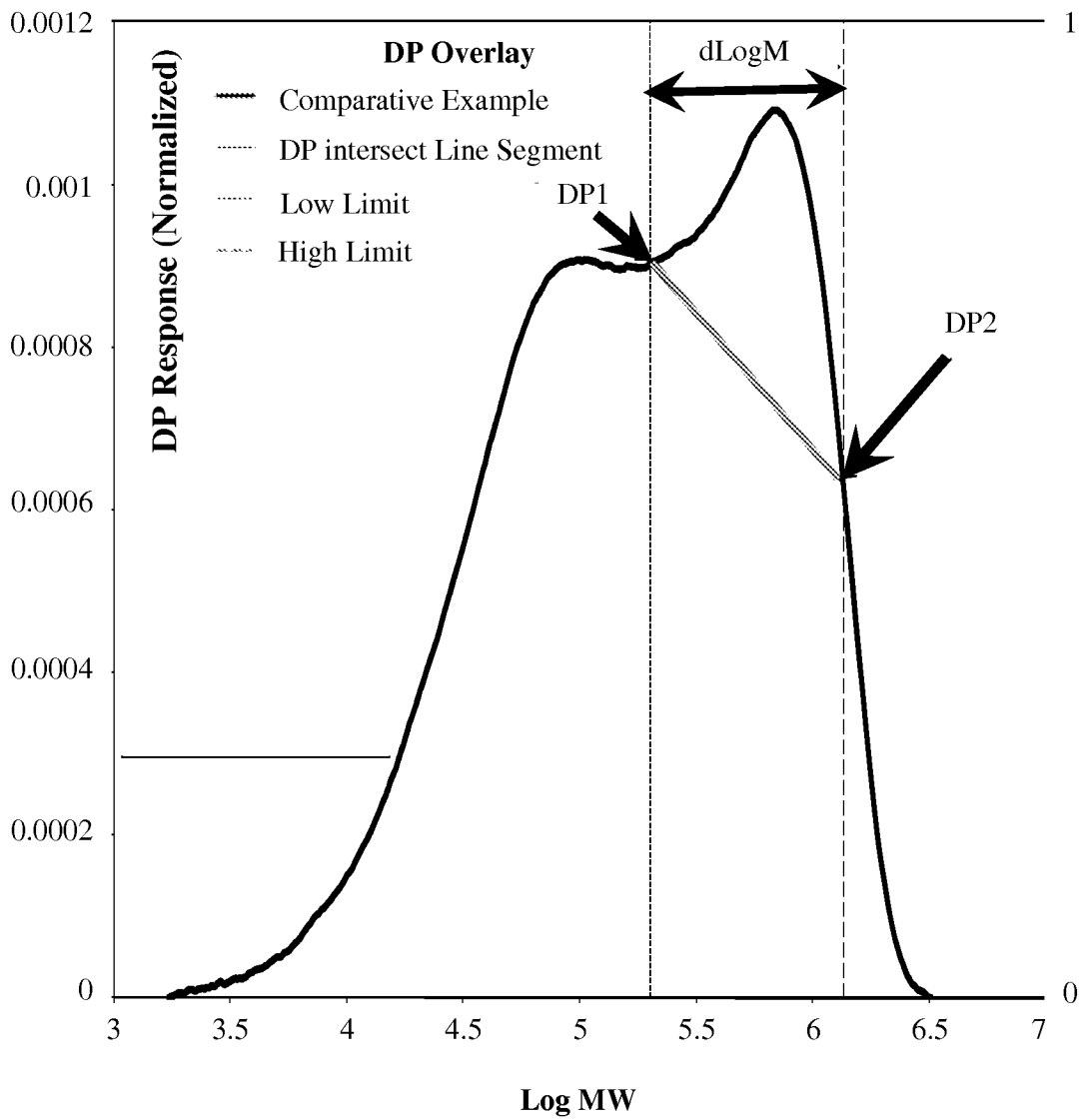
Low MW = 200,000
 High MW = 1,355,000

Slope = (DP2-DP1) / DP2 / dLogM
 DPSF = abs(Slope) + 0.001

DPP = Log (DPSF) + 2

10

FIGURE 3



5

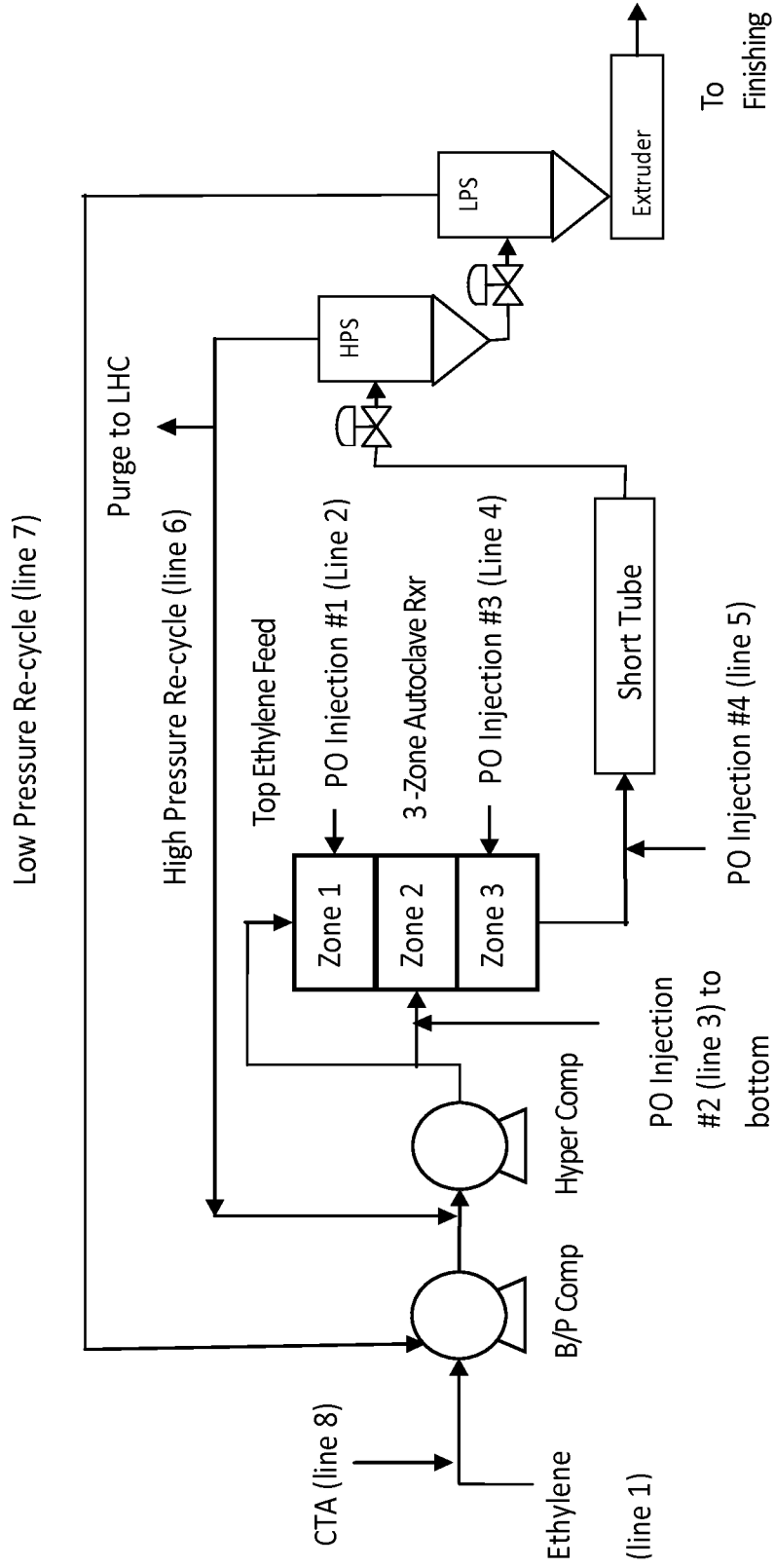
DPP Calculation

Low MW = 200,000
 High MW = 1,355,000

Slope = (DP2-DP1 / DP2 / dLogM)
 DPSF = abs(Slope) + 0.001

DPP = Log (DPSF) + 2

FIGURE 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/029652

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08F10/02 C08F2/00 C08J5/18 C08L23/04
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08F
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/019563 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; KARJALA TERESA P [US]; TICE COLLEEN) 17 February 2011 (2011-02-17) cited in the application claims; figures; tables -----	1-15
X	WO 2010/144784 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; KARJALA TERESA [US]; SAVARGAONKAR NI) 16 December 2010 (2010-12-16) cited in the application claims; examples; tables -----	1-15
X	WO 2010/042390 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; KARJALA TERESA [US]; EDDY CHRISTOPHE) 15 April 2010 (2010-04-15) cited in the application claims; examples; tables -----	1-15
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
---	---

Date of the actual completion of the international search 24 May 2013	Date of mailing of the international search report 03/06/2013
---	---

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kaumann, Edgar
--	---

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/029652

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/082393 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; KARJALA TERESA P [US]; KARDOS LORI L) 21 June 2012 (2012-06-21) cited in the application claims -----	1-15
X	WO 96/16119 A1 (DOW CHEMICAL CO [US]; KALE LAWRENCE T [US]; JAIN PRADEEP [US]; KELLEY) 30 May 1996 (1996-05-30) claims -----	1-15
A	US 2002/143123 A1 (DEKMEZIAN ARMENAG HAGOP [US] ET AL) 3 October 2002 (2002-10-03) claims -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/029652

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 2011019563	A1	17-02-2011	CA 2768705 A1	17-02-2011
			CN 102574946 A	11-07-2012
			EP 2464672 A1	20-06-2012
			JP 2013501847 A	17-01-2013
			KR 20120052295 A	23-05-2012
			SG 178309 A1	29-03-2012
			US 2012130019 A1	24-05-2012
			WO 2011019563 A1	17-02-2011

WO 2010144784	A1	16-12-2010	CA 2763077 A1	16-12-2010
			CN 102803309 A	28-11-2012
			EP 2440588 A1	18-04-2012
			JP 2012530151 A	29-11-2012
			KR 20120036832 A	18-04-2012
			SG 176776 A1	30-01-2012
			US 2010317804 A1	16-12-2010
			WO 2010144784 A1	16-12-2010

WO 2010042390	A1	15-04-2010	CA 2738475 A1	15-04-2010
			CN 102239188 A	09-11-2011
			EP 2331590 A1	15-06-2011
			JP 2012505292 A	01-03-2012
			KR 20110084905 A	26-07-2011
			US 2010087606 A1	08-04-2010
			US 2011178253 A1	21-07-2011
			WO 2010042390 A1	15-04-2010

WO 2012082393	A1	21-06-2012	NONE	

WO 9616119	A1	30-05-1996	AT 185829 T	15-11-1999
			AU 691386 B2	14-05-1998
			BR 9510328 A	02-06-1998
			CA 2205116 A1	30-05-1996
			DE 69512932 D1	25-11-1999
			DE 69512932 T2	09-03-2000
			EP 0792318 A1	03-09-1997
			ES 2137558 T3	16-12-1999
			FI 972032 A	11-07-1997
			JP 3582836 B2	27-10-2004
			JP H10509200 A	08-09-1998
			NO 972203 A	14-07-1997
			NZ 297629 A	28-01-2000
			WO 9616119 A1	30-05-1996

US 2002143123	A1	03-10-2002	AT 415427 T	15-12-2008
			EP 1448632 A1	25-08-2004
			ES 2316478 T3	16-04-2009
			US 2002143123 A1	03-10-2002
			WO 03033554 A1	24-04-2003
