PROCESS FOR THE PRODUCTION OF POLYETHYLENES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/575,922 filed April 8, 2024, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to the production of ethylene-based polymers, and more specifically, to the production of ethylene-based polymers in loop reactors.

BACKGROUND

[0003] When polyethylene copolymers are produced in a loop reactor, the relative concentrations of monomer and comonomer vary around the loop. This causes variation in the comonomer content of the polymer produced in different parts of the loop. This variation is referred to as short chain branching distribution. A higher variation of the comonomer incorporated diminishes polymer properties (e.g., causing pellet stickiness, film stickiness, lower dart impact resistance, and decreased tear strength). Accordingly, it is desired to decrease variation in the amount of monomer and comonomer incorporated into the polymer.

BRIEF SUMMARY

[0004] It has subsequently been discovered that catalyst deactivation plays a substantially more significant role in the broader short chain branching distribution than was previously thought. Previously, it was believed that catalyst half-life in a loop reactor was at least the same as catalyst recirculation time; therefore, a single catalyst injector was used. Surprisingly, it was discovered that catalyst half-life may be 50% or less of catalyst recirculation time. This short half-life, relative to recirculation time, is believed to result in excessive catalyst activity in the first half of the loop and insufficient catalyst activity in the second half of the loop, thereby causing an excessively broad short chain branching distribution. Accordingly, processes for the production of ethylene-based polymers that

mitigate the issues of excessive short chain branching and relatively short catalyst half-life are desired.

[0005] Embodiments of the present disclosure meet this need by providing a loop reactor comprising a first catalyst injection point in the first half of the loop and a second catalyst injection point in the second half of the loop. Embodiments then control one or more polymerization conditions (e.g., a ratio of catalyst introduced at the second catalyst injection point to catalyst introduced at the first catalyst injection point) such that a ratio of an amount of polymerization in the first half of the loop to an amount of polymerization in the second half is controlled, such as from 0.7 to 1.3; a ratio of the heat of polymerization in the first half to the heat of polymerization in the second half is from 0.7 to 1.3; or both. Controlling the polymerization conditions is believed to balance polymerization around the reactor, resulting in reduced concentration gradients of monomers and comonomers and a narrower short chain branching distribution.

[0006] In some embodiments, the polymerization condition which is controlled is a ratio of catalyst injected at the second catalyst injection point to catalyst injected at the first catalyst injection point. Controlling the polymerization by controlling the ratio of catalysts introduced at the two injection points in this manner is believed to be a particularly effective and inexpensive method by which to control polymerization rates.

[0007] Further embodiments of the present disclosure meet this need by providing loop reactors where the number of catalyst injection points equals the number of feed injection points. Although loop reactors with two feed injection points have been in operation for several decades now and the need to narrow short chain branching distribution has been known, it was not understood that increasing the number of catalyst injection points to equal the number of feed injection points could be a viable way to narrow short chain branching distribution. Prior attempts to narrow short chain branching distribution focused on decreasing production rates, which has adverse consequences for process economics.

[0008] According to some embodiments, a process for forming an ethylene-based polymer may comprise: introducing catalyst to a loop reactor through at least two catalyst injection points, where: the loop comprises a first half and a second half, and the first catalyst injection point is in the first half of the loop and the second catalyst injection point is in the second

half of the loop; and polymerizing the ethylene and copolymer while controlling one or more polymerization conditions such that: a ratio of an amount of polymerization in the first half to an amount of polymerization in the second half is from 0.7 to 1.3; a ratio of the heat of polymerization in the first half to the heat of polymerization in the second half is from 0.7 to 1.3; or both, thereby forming the ethylene-based polymer.

[0009] These and other embodiments are described in more detail in the Detailed Description. It is to be understood that both the foregoing general description and the following detailed description present embodiments of the presently disclosed technology, and are intended to provide an overview or framework for understanding the nature and character of the technology as it is claimed.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0010] The following detailed description of specific embodiments of the present disclosure can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

[0011] FIG. 1 schematically depicts the operation of a loop reactor, according to one or more embodiments described herein;

[0012] FIG. 2 is a HT-TGIC spectra used to determine short chain branching;

[0013] FIG. 3 is a HT-TGIC spectra for Example 1 and Comparative Example 1;

[0014] FIG. 4 is a HT-TGIC spectra for Example 2 and Comparative Example 2; and

[0015] FIG. 5 is a HT-TGIC spectra for Example 3 and Comparative Example 3.

[0016] Reference will now be made in greater detail to various embodiments, some embodiments of which are illustrated in the accompanying drawings. Whenever possible, the same reference numerals will be used throughout the drawings to refer to the same or similar parts.

DETAILED DESCRIPTION

Definitions

[0017] 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 as well as "copolymer" which refers to polymers prepared from two or more different monomer types.

[0018] "Polyethylene" or "ethylene-based polymer" shall mean polymers comprising greater than 50% by weight of units that have been derived from ethylene monomer. This includes polyethylene homopolymers or copolymers (meaning units derived from two or more monomer types). Common forms of polyethylene known in the art include Low Density Polyethylene (LDPE); Linear Low Density Polyethylene (LLDPE); Ultra Low Density Polyethylene (ULDPE); Very Low Density Polyethylene (VLDPE); single-site catalyzed Linear Low Density Polyethylene, including both linear and substantially linear low density resins (m-LLDPE); Medium Density Polyethylene (MDPE); and High Density Polyethylene (HDPE).

[0019] The term "LDPE" may also be referred to as "high pressure ethylene polymer" or "highly branched polyethylene" and is defined to mean that the polymer is partly or entirely homopolymerized or copolymerized in autoclave or tubular reactors at pressures above 14,500 psi (100 MPa) with the use of free-radical initiators, such as peroxides (*see*, for example, U.S. Patent No. 4,599,392, which is hereby incorporated by reference in its entirety). LDPE resins typically have a density in the range of 0.916 g/cm^3 to 0.930 g/cm^3.

[0020] The term "LLDPE," includes resin made using Ziegler-Natta catalyst systems as well as resin made using single-site catalysts, including, but not limited to, bis-metallocene catalysts (sometimes referred to as "m-LLDPE"), phosphinimine, and constrained geometry catalysts, and resins made using post-metallocene, molecular catalysts, including, but not limited to, bis(biphenylphenoxy) catalysts (also referred to as polyvalent aryloxyether catalysts). LLDPE includes linear, substantially linear, or heterogeneous ethylene-based copolymers. LLDPEs contain less long chain branching than LDPEs and include the substantially linear ethylene polymers, which are further defined in U.S. Patent No. 5,272,236, U.S. Patent No. 5,278,272, U.S. Patent No. 5,582,923 and U.S. Patent No. 5,733,155 each of which are incorporated herein by reference in their entirety; the

homogeneously branched linear ethylene polymer compositions such as those in U.S. Patent No. 3,645,992 which is incorporated herein by reference in its entirety; the heterogeneously branched ethylene polymers such as those prepared according to the process disclosed in U.S. Patent No. 4,076,698 which is incorporated herein by reference in its entirety; and blends thereof such as those disclosed in U.S. Patent No. 3,914,342 and U.S. Patent No. 5,854,045 which are incorporated herein by reference in their entirety. The LLDPE resins can be made via gas-phase, solution-phase, or slurry polymerization or any combination thereof, using any type of reactor or reactor configuration known in the art.

Loop Reactors

[0021] Referring now to FIG. 1, in some embodiments, a loop reactor 100 may comprise a continuous pipe that runs in a loop 102. Ethylene and copolymer may polymerize via a solution phase polymerization process, in the presence of a catalyst, within the loop 102 of continuous pipe. The loop 102 may comprise a first half 104, and a second half 110.

[0022] In some of the embodiments depicted in FIG. 1, the first half 104 is the space between an outlet 106b of a second heat exchanger 106 and an outlet 108b of first heat exchanger 108; and the second half 110 is the space between an outlet 108b of the first heat exchanger 108 and an outlet 106b of the second heat exchanger 106.

[0023] Catalyst may be introduced to the loop reactor 100 via a first catalyst injection point 112. Ethylene and comonomer may be introduced to the loop reactor 100 via a first feed injection point 114. In some embodiments, ethylene and comonomer may be introduced through a single injection point. In alternate embodiments, ethylene and comonomer may be introduced through separate injection points. In either case, ethylene and comonomer may be introduced within the first half 104 at the first feed injection point 114. It should be understood that each of ethylene, comonomer, and catalyst may be introduced to the first half 104 by more than one injection point (e.g., there may be 1, 2, 3, or 4 ethylene injection points in the first half 104; 1, 2, 3, or 4 comonomer injection points in the first half 104; and/or 1, 2, 3, or 4 catalyst injection points in the first half 104). Moreover, the location of the first feed injection point 114 and the first catalyst injection point 112 within the first half 104 is not particularly limited, such that the first feed injection point 114 and the first catalyst injection point 112 need not be located adjacent to a heat exchanger. In some embodiments

not depicted in the figures, a single, combined injector may be utilized to introduce the ethylene, comonomer, and catalyst to the first half 104. In such embodiments, the first feed injection point 114 may also be the first catalyst injection point 112.

[0024] The catalyst, ethylene, and comonomer may polymerize, within loop 102, to form an ethylene-based polymer and release heat. Still within loop 102, the catalyst, ethylene, comonomer, and ethylene may pass to a first heat exchanger 108. Within the first heat exchanger 108, heat may be transferred from the loop 102 to first heat exchanger cold feed 116, thereby forming first heat exchanger hot effluent 118. The catalyst, ethylene, and comonomer may then pass to second half 110, which begins at the outlet 108b of the first heat exchanger 108.

[0025] In second half 110, additional catalyst may be introduced to loop 102 via a second catalyst injection point 120. Additional ethylene and comonomer may be introduced to loop 102 via a second feed injection point 122. In some embodiments, ethylene and comonomer may be introduced through a single injection point. In alternate embodiments, ethylene and comonomer may be introduced through separate injection points. In either case, the ethylene and comonomer may be introduced within the second half 110 at the second feed injection point 122. It should be understood that each of ethylene, comonomer, and catalyst may be introduced to the second half 110 by more than one injection point (e.g., there may be 1, 2, 3, or 4 ethylene injection points in the second half 110; 1, 2, 3, or 4 comonomer injection points in the second half 110; and/or 1, 2, 3, or 4 catalyst injection points in the second half 110). Moreover, the location of the second feed injection point 122 and the second catalyst injection point 120 within the second half 110 is not particularly limited, such that the second feed injection point 122 and the second catalyst injection point 120 need not be located adjacent to a heat exchanger. In some embodiments not depicted in the figures, a single, combined injector may be utilized to introduce the ethylene, comonomer, and catalyst to the second half 110. In such embodiments, the second feed injection point 122 may also be the second catalyst injection point 120.

[0026] In embodiments, the number of feed injection points may equal the number of catalyst injection points. For example, the loop reactor 100 may include two feed injection points and two catalyst injection points, three feed injection points and three catalyst injection

points, four feed injection points and four catalyst injection points, or even five feed injection points and five catalyst injection points. In embodiments, the number of ethylene injection points may equal the number of catalyst injection points. For example, the loop reactor 100 may include two ethylene injection points and two catalyst injection points, three ethylene injection points and three catalyst injection points, four ethylene injection points and four catalyst injection points, or even ethylene feed injection points and five catalyst injection points.

[0027] The produced ethylene-based polymer may be removed from loop reactor 100 via reactor outlet 124.

Processes for Producing Ethylene-Based Polymers

[0028] Embodiments of the present disclosure are directed to a process for forming an ethylene-based polymer. Still referring to FIG. 1, the process may comprise introducing catalyst to a loop reactor 100 through at least two catalyst injection points 112, 120. The loop reactor 100 may comprise a first half 104 and a second half 110. The first catalyst injection point 112 may be positioned in the first half 104 and the second catalyst injection point 120 may be positioned in the second half 110.

[0029] The process may further comprise introducing ethylene and a comonomer to the loop reactor 100 through at least two feed injection points 114, 122. The first feed injection point 114 may be positioned in the first half 104 of the loop 102 and the second feed injection point 122 may be positioned in the second half 110 of the loop 102.

[0030] The comonomer may comprise olefins, such as C_3-C_{14} olefins, such as C_3-C_{14} α-olefins. Contemplated comonomers include, by way of example but not limitation, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, and 1-tetradecene.

[0031] The catalyst may comprise conventional solution polyethylene polymerization catalysts. By way of example and not limitation, the catalyst may comprise Ziegler-Natta catalysts, metallocene catalysts, and post-metallocene catalysts.

[0032] The process may comprise polymerizing the ethylene and comonomer to form the ethylene-based polymer. In embodiments, the process may comprise polymerizing the ethylene and comonomer while controlling one or more polymerization conditions (e.g., a ratio of catalyst injected at the second catalyst injection point 120 to catalyst injected at the first catalyst injection point 112) such that a ratio of an amount of polymerization in the first half 104 to an amount of polymerization in the second half 110 is from 0.7 to 1.3, such as from 0.8 to 1.2, from 0.9 to 1.1, from 0.95 to 1.05, from 0.7 to 0.8, from 0.8 to 0.9, from 0.9 to 1.0, from 1.0 to 1.1, from 1.1 to 1.2, from 1.2 to 1.3, or any combination of two or more of these ranges. Without being limited by theory, it is believed that controlling the amount of catalyst injected into each half of the loop reactor 100, such that the amount of polymerization in the first half 104 and the second half 110 is relatively even, such as from 0.7 to 1.3, results in narrower short chain branching distribution and improved material properties in the resulting ethylene-based polymer.

[0033] In embodiments, the process may comprise controlling one or more polymerization conditions (e.g., a ratio of catalyst injected at the second catalyst injection point 120 to catalyst injected at the first catalyst injection point 112) such that a ratio of the heat of polymerization in the first half 104 to the heat of polymerization in the second half 110 is from 0.7 to 1.3. such as from 0.8 to 1.2, from 0.9 to 1.1, from 0.95 to 1.05, from 0.7 to 0.8, from 0.8 to 0.9, from 0.9 to 1.0, from 1.0 to 1.1, from 1.1 to 1.2, from 1.2 to 1.3, or any combination of two or more of these ranges. Without being limited by theory, it is believed that controlling the amount catalyst to each half of the loop reactor 100, such that the heat of polymerization in the first half 104 and the second half 110 is relatively even, such as from 0.7 to 1.3, results in narrower short chain branching distribution and improved material properties in the resulting ethylene-based polymer.

[0034] The ratio of the amount and/or heat of polymerization in the first half 104 to the amount and/or heat of polymerization in the second half 110 may be controlled by controlling the amount of catalyst fed to each of the first half 104 and the second half 110. In embodiments, the ratio of catalyst injected at the second catalyst injection point 120 to the catalyst injected at the first catalyst injection point 112 is from 0.7 to 1.3, such as from 0.8 to 1.2, from 0.9 to 1.1, from 0.95 to 1.05, from 0.7 to 0.8, from 0.8 to 0.9, from 0.9 to 1.0,

from 1.0 to 1.1, from 1.1 to 1.2, from 1.2 to 1.3, or any combination of two or more of these ranges.

[0035] In embodiments, the process may comprise measuring the heat of polymerization in the first half 104 and the heat of polymerization in the second half 110. The process may then comprise controlling the amount of catalyst to the first catalyst injection point 112 and the second catalyst injection point 120, based on the ratio of heat generated in the first half 104 and the heat generated in the second half 110. In embodiments, the process may comprise increasing the proportion of catalyst to the second catalyst injection point 120, if the ratio of the heat of polymerization in the first half 104 to the heat of polymerization in the second half 110 is greater than 1.2. In embodiments, the process may comprise decreasing the proportion of catalyst to the second catalyst injection point 120, if the ratio of the heat of polymerization in the first half 104 to the heat of polymerization in the second half 110 is less than 0.8.

[0036] It has been discovered that part of the reason for the broader comonomer distribution is related to catalyst deactivation, as quantified by the measurement catalyst half-life. Catalyst half-life refers to the time it takes for 50% of the catalyst in the reactor to be deactivated. Without being limited by theory, when only one catalyst injector is used in the loop reactor 100, more material is made in the first half 104 (nearest the catalyst injection) and less material in the second half 110 as a result of catalyst deactivation. This is believed to cause over-conversion of ethylene in the first half 104 where the catalyst is most active. When ethylene is over-converted, a polymer with high comonomer content is produced. This material with the high comonomer content is a cause of sticky pellets and sticky films. In embodiments, a half-life of the catalyst in the loop reactor 100 is less than 80% of a recirculation time of the catalyst in the loop reactor 100, such as less than 70%, less than 60%, or less than 50%. Generally, when catalyst half- lives relative to recirculation times are shorter, the importance of multiple injection points increases.

[0037] In embodiments, polymerizing the ethylene and comonomer may occur at a temperature of from 180 °C to 210 °C, such as from 180 °C to 185 °C, from 185 °C to 190 °C, from 190 °C to 195 °C, from 195 °C to 200 °C, from 200 °C to 205 °C, from 205 °C to 210 °C, or any combination of two or more of these ranges. Generally, it is believed that

polymerizing at too low of a temperature, such as below 180 °C results in lower production rates and undesirably increased polymer solution viscosity. Generally, it is believed that polymerizing at too high of a temperature, such as above 210 °C, results in decreased catalyst activity and increased cost. In embodiments, polymerizing the ethylene and comonomer may occur in the presence of a solvent. Contemplated solvents include linear or paraffinic hydrocarbon solvents.

[0038] As shown in FIG. 1, the loop reactor 100 may comprise a first heat exchanger 108 and a second heat exchanger 106. The first catalyst injection point 112 and first feed injection point 114 may be upstream of the first heat exchanger 108 and downstream of the second heat exchanger 106. The second catalyst injection point 120 and the second feed injection point 122 may be upstream of the second heat exchanger 106 and downstream of the first heat exchanger 108.

[0039] In embodiments, processes may comprise controlling the ratio of catalyst injected at the first catalyst injection point 112 to the catalyst injected at the second catalyst injection point 120 such that a ratio of heat extracted at the second heat exchanger to heat extracted at the first heat exchanger may be from 0.7 to 1.3, such as from 0.8 to 1.2, from 0.9 to 1.1, from 0.95 to 1.05, from 0.7 to 0.8, from 0.8 to 0.9, from 0.9 to 1.0, from 1.0 to 1.1, from 1.1 to 1.2, from 1.2 to 1.3, or any combination of two or more of these ranges. Generally, controlling the ratio of catalyst injected at the first catalyst injection point 112 to the catalyst injected at the second catalyst injection point 120 based upon the ratio of heat extracted at the two heat exchanges may enable easy and cost effective monitoring of the reaction, without the need for additional monitoring equipment or simulations.

[0040] The ratio of catalyst injected at the second catalyst injection point 120 to the catalyst injected at the first catalyst injection point 112 may be a mass flow ratio or a volumetric flow ratio. The catalyst injected at the second catalyst injection point 120 may be the same as the catalyst injected at the first catalyst injection point 112.

Ethylene-Based Polymers

[0041] In embodiments, less than 8 wt. % of the polymer has a high temperature thermal gradient interaction chromatography (also referred to as "HT-TGIC" or "TGIC") elution

temperature less than 80 °C. For example, less than 7 wt. %, less than 6.5 wt. %, less than 6.0 wt. %, less than 5.5 wt. %, less than 5.3 wt. %, less than 5.0 wt. %, less than 4.8 wt. %, less than 4.6 wt. %, or even less than 4.3 wt. % of the polymer may have a TGIC elution temperature less than 80 °C.

[0042] In embodiments, the ethylene-based polymer has a density of from 0.85 to 0.94 g/cc, such as from 0.85 to 0.87 g/cc, from 0.87 to 0.89 g/cc, from 0.89 to 0.91 g/cc, from 0.91 to 0.93 g/cc, from 0.93 to 0.94 g/cc, or any combination of two or more of these ranges.

[0043] In embodiments, the ethylene-based polymer has a melt index (I_2) of from 0.2 to 2000 dg/min, such as from 0.2 to 0.5 dg/min, from 0.5 to 5 dg/min, from 5 to 20 dg/min, from 20 to 50 dg/min, from 50 to 200 dg/min, from 200 to 500 dg/min, from 500 to 1000 dg/min, from 1000 to 2000 dg/min, or any combination of two or more of these ranges.

TEST METHODS

TGIC

[0044] High temperature thermal gradient interaction chromatography (HT-TGIC) was determined according to the methods disclosed in U.S. Pat. No. 9902791B2, the entirety of which in incorporated by reference herein.

SCBD

[0045] The TGIC chromatogram is related to comonomer content and its distribution. The distribution gets broader with the increase in comonomer content according to Stockmeyer equation. It can also be related to the number of catalyst active sites (Soares et al., Polyolefin reaction engineering Wiley-VCH, Polyolefin Microstructural modeling, Chapter 6) or the process conditions. (For general knowledge, please refer to Stregel, et al., "Modern size-exclusion liquid chromatography, Wiley, 2nd edition, Chapter 3).

[0046] The broadness of the chemical composition distribution can be quantified by the ratio of broadness of TGIC profile at different maximum heights, for example, the ratio of the broadness of TGIC profile at 1/4 maximum height to the broadness of TGIC profile at 1/4 maximum.

[0047] The procedure of TGIC profile width (@1/4th maximum height) is the following:

1. Run samples and the Eicosane/iPP/homopolymer polyethylene mixture in the same run queue according to the TGIC method above. If not in same run queue, samples may be run over a very short time period in the same TGIC instrument (to minimize variability in IR detector response and broadness). In this case, the peak width at 1/4 of HDPE in the Eicosane/iPP/homopolymer polyethylene mixture must be <1%RSD to be able to compare TGIC profile width of the samples of interest;

2. Generate TGIC chromatograms dWi/dT versus elution temperature (T);

3. For each sample, obtain the maximum height from the TGIC chromatogram (dWi/dTi) by searching each data point for the highest intensity from 35.0 °C to 170.0 °C, the corresponding elution temperature of TGIC chromatogram at the maximum height is defined as profile temperature (Tp). The profile width (1/4) is defined as the temperature difference between the front temperature and the rear temperature at 1/4 of the maximum height, the front temperature at the 1/4 of the maximum height is searched forward from 35.0°C, while the rear temperature at the 1/4 of the maximum height is searched backward from 170.0°C.

4. Calculate of the peak width of HDPE at 1/4th of HDPE peak height (PeakWidth@1/4th) from Eicosane/iPP/HDPE (see FIG. 2). The peak elution temperature of homopolymer polyethylene HDPE is set at 150 °C.

5. Broadness of TGIC profile at 1/4th maximum height is defined as:

$$Broadness\ of\ TGIC\ profile\ (at\ 1/4th\ maximum\ height) = \frac{Profile\ width\ \left(at\ \frac{1}{4}\ maximum\ height\right)}{\text{PeakWidth@}\frac{1}{4}\text{ of HDPE}} X \frac{Tp}{150}$$

Density

[0048] Samples for density measurement are prepared according to ASTM D 1928. Polymer samples are pressed at 190 °C and 30,000 psi for three minutes, and then at 21 °C and 207

MPa for one minute. Measurements are made within one hour of sample pressing using ASTM D792, Method B.

Melt Index (I_2) and (I_{10})

[0049] Melt index, or I_2, (grams/10 minutes or dg/min) is measured in accordance with ASTM D 1238, Condition 190 °C/2.16 kg, Procedure B. Melt index, or I_{10}, (grams/10 minutes or dg/min) is measured in accordance with ASTM D 1238, Condition 190 °C/10 kg, Procedure B.

EXAMPLES

[0050] The following examples illustrate features of the present disclosure but are not intended to limit the scope of the disclosure. The following experiments analyzed the performance of embodiments of the process for forming ethylene-based polymers described herein.

[0051] Experiments were performed in a continuously operated 40 gallon loop reactor containing 2 shell and tube exchangers to remove the heat of polymerization. Ethylene, octene, hydrogen, and Isopar-E solvent were added to the reactor at a temperature of 40 °C at a first feed injection point in the first half of the reactor and at a second feed injection point in the second half of the reactor. The levels of these four species were varied to produce a final polymer at a rate of 450 lb/hr, a melt index of 1.0 dg/min, and a density of 0.870 g/cc at a reactor polymer concentration of 29%. Catalyst and cocatalyst were added to convert 91% of the ethylene added to the reactor. Catalyst was added at either a single injection point or split between a first catalyst injection point in the first half of the reactor and at a catalyst injection point in the second half of the reactor. The temperature of the reactor was controlled by adjusting the temperature of the cooling water utilized in the two exchangers. The recirculation time in the reactor loop for all these experiments was 98 seconds.

[0052] Process conditions are given in Table 1 when the catalyst was catalyst A. Catalyst A is a bis-biphenyl phenoxy catalyst, depicted as Formula I below. Catalyst A was activated with 1.2 equivalents of the cocatalyst (Amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-)) (CAS# 200644-82-2).

Formula I

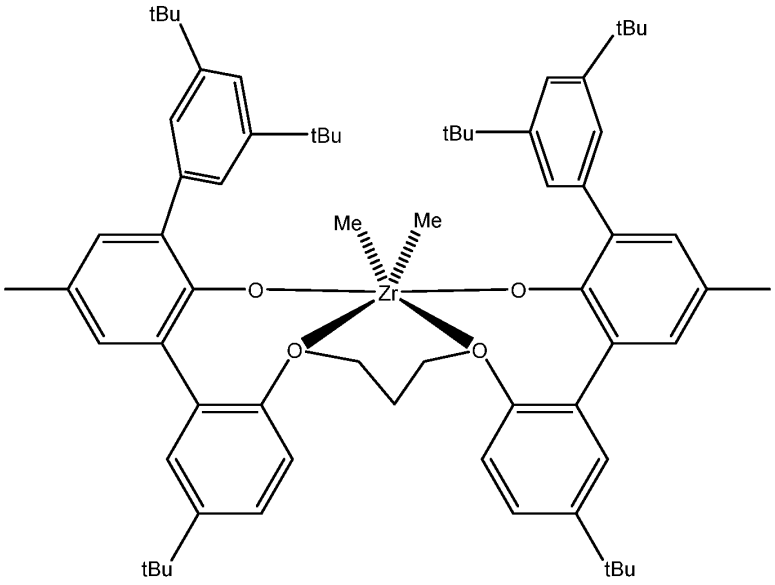


Table 1

	# catalyst injectors used	Reactor Temp (°C)	Heat balance	Calculated catalyst half-life (s)	Polymer Broadening (PB)	Wt. % <80 °C
C-1	1	190	1.52	136	5.2	4.89
E-1	2	190	1.04	136	4.8	4.35
C-2	1	200	1.31	46	5.4	5.88
E-2	2	200	0.79	46	4.8	3.88

[0053] The TGIC spectra of C-1 and E-1 are provided in FIG. 3. TGIC spectra of C-2 and E-2 are provided in FIG. 4. As can be seen from Table 1, FIG. 3, and FIG. 4, the addition of a second catalyst injector narrows the polymer short chain branching distribution, as indicated in a decrease of both the polymer broadening and the fraction of material with a TGIC temperature <80 °C. When the reactor temperature is increased from 190 °C to 200 °C, the catalyst half-life is reduced and the effect of the second catalyst injector is more pronounced.

[0054] The experiment was repeated with catalyst B. Catalyst B is a bis-biphenyl phenoxy catalyst, depicted as Formula II below. Catalyst B was activated with 1.2 equivalents of the cocatalyst (Amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl) borate(1-)) (CAS# 200644-82-2).Process conditions are given in Table 2.

Formula II

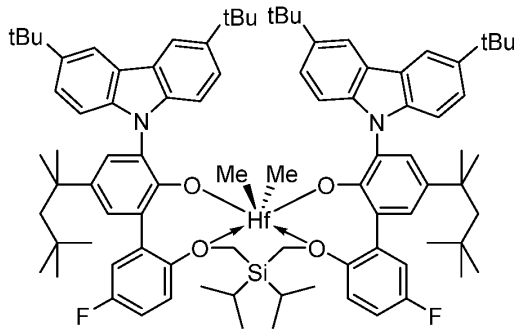


Table 2

	# catalyst injectors used	Reactor Temp (°C)	Heat balance	Calculated catalyst half-life (s)	PB	Wt. % <80 C
Comp 3	1	190	1.91	54	4.8	8.90
Inventive 3	2	190	0.97	54	4.1	4.69

[0055] The TGIC spectra of C-3 and E-3 are provided in FIG. 5. As can be seen from FIG. 5 and Table 2, the addition of a second catalyst injector narrows the polymer short chain branching distribution, as indicated in a decrease of both the polymer broadening and the fraction of material with a TGIC temperature <80 °C. As catalyst B has a relatively short half-life, the effect of a second catalyst injector is relatively pronounced.

CLAIMS

1. A process for forming an ethylene-based polymer, the process comprising:

introducing catalyst to a loop reactor through at least two catalyst injection points, where:

the loop reactor comprising a loop, the loop comprising a first half and a second half, and

a first catalyst injection point is in the first half of the loop and a second catalyst injection point is in the second half of the loop;

introducing ethylene and a comonomer to the loop reactor through at least two feed injection points, where a first feed injection point is in the first half of the loop and a second feed injection point is in the second half of the loop; and

polymerizing the ethylene and copolymer while controlling one or more polymerization conditions such that:

a ratio of an amount of polymerization in the first half of the loop to an amount of polymerization in the second half of the loop is from 0.7 to 1.3;

a ratio of a heat of polymerization in the first half of the loop to a heat of polymerization in the second half of the loop is from 0.7 to 1.3; or

both, thereby forming the ethylene-based polymer.

2. The process of claim 1, wherein the polymerization condition controlled is a ratio of catalyst injected at the second catalyst injection point to catalyst injected at the first catalyst injection point.

3. The process of claim 2, the ratio of catalyst injected at the second catalyst injection point to the catalyst injected at the first catalyst injection point is from 0.7 to 1.3.

4. The process of any one of claims 1-3, wherein the one or more polymerization conditions are controlled such that a ratio of the heat of polymerization in the first half to the heat of polymerization in the second half is from 0.7 to 1.3.

5. The process of any one of claims 1-4, wherein the number of catalyst injection points equals the number of feed injection points.

6. The process of any one of claims 1-5, wherein:

the loop reactor comprises a first heat exchanger and a second heat exchanger,

the first catalyst injection point and the first feed injection point are upstream of the first heat exchanger and downstream of the second heat exchanger, and

the second catalyst injection point and the second feed injection point are upstream of the second heat exchanger and downstream of the first heat exchanger.

7. The process of claim 6, a ratio of heat extracted at the second heat exchanger to heat extracted at the first heat exchanger is from 0.7 to 1.3.

8. The process of any one of claims 1-7, wherein a half-life of the catalyst in the loop reactor is less than 80% of a recirculation time of the catalyst in the loop reactor.

9. The process of any one of claims 1-8, wherein the ethylene and copolymer polymerization conditions are controlled such that:

the ratio of the amount of polymerization in the first half of the loop to the amount of polymerization in the second half of the loop is from 0.9 to 1.1;

the ratio of the heat of polymerization in the first half of the loop to the heat of polymerization in the second half of the loop is from 0.9 to 1.1; or both.

10. The process of any one of claims 1-9, wherein less than 4.8 wt. % of the polymer has a TGIC elution temperature less than 80 °C.

11. The process of any one of claims 1-10, wherein the loop reactor has an operating temperature of from 180 °C to 210 °C.

12. The process of any one of claims 1-11, wherein the comonomer comprises C_3-C_{14} olefins.

13. The process of any one of claims 1-12, wherein the ethylene-based polymer has a density of from 0.85 to 0.94 g/cc.

14. The process of any one of claims 1-13, wherein the ethylene-based polymer has a melt index of from .2 to 2000 dg/min.

15. The process of any one of claims 1-14, wherein polymerizing the ethylene and copolymer while controlling one or more polymerization conditions comprises:

determining the ratio of the heat of polymerization in the first half of the loop to the heat of polymerization in the second half of the loop; and

if the ratio of the heat of polymerization in the first half of the loop to the heat of polymerization in the second half of the loop is greater than 1.2, increasing the proportion of catalyst injected at the second catalyst injection point, or

if the ratio of the heat of polymerization in the first half of the loop to the heat of polymerization in the second half of the loop is less than 0.8, decreasing the proportion of catalyst injected at the second catalyst injection point.