radicals or dienes to initiate long-chain branching, the branching may become too numerous, thereby causing gelling and reactor fouling. The reincorporation mechanism does not produce much branching, and branching can only occur after the polymer strand is produced, thereby further limiting the amount of branching that can occur.

[0006] An increased amount of long-chain branching (LCB) provides an increase in melt processing properties. Long-chain branched material (e.g., low density polyethylene, LDPE) is added to LLDPE as a processing aid. In general, LDPE has good processing properties but films made from it have poor physical properties such as tear or dart strength. Films made from linear low density polyethylene (LLDPE) have good physical properties such as tear or dart strength but cannot be effectively processed. Blending of some amount of LDPE is required for processing (melt strength, shear thinning) but these reduce the physical properties of LLDPE films. When blending LLDPE and LDPE, researchers are balancing processability and physical properties, while never achieving ideal values for both.

SUMMARY

[0007] Ongoing needs exist to produce a polymer composition having a high melt strength and normal to low viscosity as indicated by the melt index, which provides better processability yet allow the polymers to be formed without fouling in a reactor. Thus, the process and ethylene-based polymers of this disclosure seek to form long-chain branching without causing the ethylene-based polymer to gel or foul reactors.

[0008] This disclosure is directed to ethylene-based polymers. The ethylene-based polymer are polymerized units derived from ethylene, diene, and optionally, one or more C_3−C_{12} α-olefins. The ethylene-based polymer includes a melt viscosity ratio ($V_{0.1}/V_{100}$) at 190 °C greater than 20. The $V_{0.1}$ is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 0.1 radians/second, and the V_{100} is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 100 radians/second. Additionally, the ethylene-based polymer includes an average g' greater than 0.86, where the average g' is an intrinsic viscosity ratio determined by gel permeation chromatography using a triple detector.

[0008a] In one aspect, there is provided an ethylene-based polymer comprising polymerized units derived from ethylene, diene, and one or more C_3−C_{12} α-olefins, wherein the ethylene-based polymer comprises: a melt viscosity ratio ($V_{0.1}/V_{100}$) at 190 °C greater than 20,

where $V_{0.1}$ is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 100 radians/second; and an average g' greater than 0.860, where the average g' is an intrinsic viscosity ratio determined by gel permeation chromatography using a triple detector, wherein the ethylene-based polymer has a conventional molecular weight distribution (MWD) of 1 to 10; and wherein the diene is unconjugated and acyclic.

[0008b] In another aspect, there is provided an ethylene-based polymer comprising polymerized units derived from ethylene, diene, and optionally one or more C_3–C_{12} α-olefins, wherein the ethylene-based polymer comprises: a melt strength greater than 10 cN (Rheotens device, 190°C, 2.4 mm/s^2, 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s^{-1}, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle); and an average g' greater than 0.860, where the average g' is an intrinsic viscosity ratio determined by gel permeation chromatography using a triple detector; wherein the ethylene-based polymer has a conventional molecular weight distribution (MWD) of 1 to 10; and wherein the diene is unconjugated and acyclic.

[0009] In some examples of this disclosure, the ethylene-based polymer are polymerized units derived from ethylene, diene, and one or more C_3–C_{12} α-olefins. The ethylene-based polymer includes a melt strength greater than 10 cN (Rheotens device, 190°C, 2.4 mm/s^2, 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s^{-1}, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle). Additionally, ethylene-based polymer includes an average g' greater than 0.86. The average g' is an intrinsic viscosity ratio determined by gel permeation chromatography using a triple detector.

BRIEF DESCRIPTION OF FIGURES

[0010] FIG. 1 is a graphical depiction of the molecular weight of a polymer as the number of branching methines per 1000 carbons increase.

[0011] FIG. 2 is a graphical model predicted dependence of the molecular weight distribution (MWD) curve on branching level.

[0012] FIG. 3 is a molecular weight distribution (MWD) curve of a two-catalyst bimodal ethylene-based polymer distribution with and without diene.

[0013] FIG. 4 is a Mark-Houwink-Sakurada plot for a conventionally long-chain branching (LCB) polymer and an LDPE, specifically DOW™ LDPE 662I.

[0014] FIG. 5 is an illustration of an ethylene-based ladder polymer, in which the polymer backbone is depicted as solid lines, and the long chain branches are depicted by dotted lines. This illustration provides a visual depiction of the difference in molecular weights calculated by conventional standard verses absolute weight average molecular weight (MW) for the long-chain branched polymers of this disclosure.

[0015] FIG. 6 is a Mark-Houwink-Sakurada plot, which shows the definition of parameters and variables that characterize the long-chain branched polymers of this disclosure in the Mark-Houwink-Sakurada plot.

[0016] FIG. 7 are Mark-Houwink-Sakurada plots of a series of bimodal ethylene-based polymers where the low MW fraction is produced by a single-chain catalyst and the high MW fraction is produced by the dual-chain catalyst.

CLAIMS

1. An ethylene-based polymer comprising polymerized units derived from ethylene, diene, and one or more C_3–C_{12} α-olefins, wherein the ethylene-based polymer comprises:
a melt viscosity ratio ($V_{0.1}/V_{100}$) at 190 °C greater than 20, where $V_{0.1}$ is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 100 radians/second; and
an average g' greater than 0.860, where the average g' is an intrinsic viscosity ratio determined by gel permeation chromatography using a triple detector,
wherein the ethylene-based polymer has a conventional molecular weight distribution (MWD) of 1 to 10; and
wherein the diene is unconjugated and acyclic.

2. An ethylene-based polymer comprising polymerized units derived from ethylene, diene, and optionally one or more C_3–C_{12} α-olefins, wherein the ethylene-based polymer comprises:
a melt strength greater than 10 cN (Rheotens device, 190°C, 2.4 mm/s^2, 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s^{-1}, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle); and
an average g' greater than 0.860, where the average g' is an intrinsic viscosity ratio determined by gel permeation chromatography using a triple detector;
wherein the ethylene-based polymer has a conventional molecular weight distribution (MWD) of 1 to 10; and
wherein the diene is unconjugated and acyclic.

3. The ethylene-based polymer of claim 1, wherein the ethylene-based polymer has a melt strength of greater than 10 cN (Rheotens device, 190°C, 2.4 mm/s^2, 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s^{-1}, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle).

4. The ethylene-based polymer of claim 2, wherein the ethylene-based polymer has a melt viscosity ratio ($V_{0.1}/V_{100}$) at 190 °C is greater than 20, where $V_{0.1}$ is the viscosity of the

ethylene-based polymer at 190 °C at a frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 100 radians/second.

5. The ethylene-based polymer of any preceding claim, wherein the diene comprises 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, dimethyldivinylsilane, dimethyldiallylsilane, dimethylallylvinylsilane.

6. The ethylene-based polymer of any preceding claim, wherein the ethylene-based polymer comprises a low molecular weight polymer fraction and a high molecular weight polymer fraction, wherein the low molecular weight polymer fraction and the high molecular weight polymer fraction each comprise polymerized units derived from ethylene, diene, and one or more C_3–C_{12} α-olefins.

7. The ethylene-based polymer of claim 6, wherein the high molecular weight polymer fraction comprises 0.5 to 30 % by weight of the polymer.

8. The ethylene-based polymer of claim 7, wherein the high molecular weight polymer fraction comprises between 1 and 15 % by weight of the polymer.

9. The ethylene-based polymer of any preceding claim, wherein the MI is greater than 0.1, wherein MI is the melt index in g/10min according to ASTM D1238.

10. The ethylene-based polymer of any preceding claim, wherein the MI is greater than 1, wherein MI is the melt index in g/10min according to ASTM D1238.

11. The ethylene-based polymer of any preceding claim, wherein the average g' is greater than 0.88.

12. The ethylene-based polymer of any preceding claim, wherein the melt strength is greater than 20 cN (Rheotens device, 190°C, 2.4 mm/s^2, 120 mm from the die exit to the center of the wheels, extrusion rate of 38.2 s^{-1}, capillary die of 30 mm length, 2 mm diameter and 180° entrance angle).

13. The ethylene-based polymer of any preceding claim, wherein the melt viscosity ratio ($V_{0.1}/V_{100}$) at 190 °C is greater than 25, where $V_{0.1}$ is the viscosity of the ethylene-based

polymer at 190 °C at a frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at a frequency of 100 radians/second.

14. The ethylene-based polymer of any preceding claim, wherein the ethylene-based polymer has a weight averaged molecular weight (M_w) of less than or equal to 250,000 Daltons, as determined by absolute gel permeation chromatography.