PROCESS OF POLYMERIZING TETRA-FUNCTIONAL LONG-CHAIN BRANCHED POLYOLEFIN RESINS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/738,621 filed on September 28, 2018, the entire disclosure of which is hereby incorporated by reference.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to polymer compositions having long-chain branches and the process by which the polymer compositions are synthesized.

BACKGROUND

[0003] Olefin based polymers, such as polyethylene and polypropylene, are produced via various catalyst systems. Selection of such catalyst systems used in the polymerization process of the olefin based polymers is an important factor contributing to the characteristics and properties of such olefin based polymers.

[0004] Polyethylene and polypropylene are manufactured for a wide variety of articles. The polyethylene and polypropylene polymerization process can be varied in a number of respects to produce a wide variety of resultant polyethylene resins having different physical properties that render the various resins suitable for use in different applications. The amount of short-chain branching in a polyolefin affects the physical properties of that polyolefin. The effect of branching on properties of polyethylene depends on the length and the amount of branches. Short branches mainly influence the mechanical and thermal properties. As the short-chain branching frequency increases, the polymer is less able to form lamellar crystals, and the mechanical and thermal properties diminish. Small amounts of long-chain branching can alter the polymer processing properties significantly.

[0005] To form long-chain branching, a vinyl or terminal double bond of a polymer chain is incorporated into a new polymer chain. Reincorporation of vinyl terminated polymers and introducing a diene comonomer are two mechanisms by which a vinyl group on a polymer strand is incorporated into a second polymer strand. Additionally, long-chain branching is

induced via radicals. It is difficult to control the amount of branching in all three mechanisms. When using 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.

SUMMARY

[0006] Embodiments of this disclosure include processes for synthesizing long-chain branched copolymers. The process includes contacting together one or more C_2-C_{14} alkene monomers, at least one diene or polyene, optionally a solvent, and a multi-chain catalyst. The multi-chain catalyst includes a plurality of polymerization sites and produces at least two polymer chains of the C_2-C_{14} alkene monomers, each polymer chain polymerizing at one of the polymerization sites. The process synthesizes the long-chain branched polymers by connecting the two polymer chains with the diene or polyene, the joining of the two polymer chains being performed in a concerted manner during the polymerization.

[0007] Various embodiments of the process include polymerizations that occur in a solution polymerization reactor or a particle forming polymerization reactor such as a slurry reactor or a gas phase reactor, wherein the molecular or solid-supported catalyst is delivered to the reaction media or developed in the reaction media, wherein the reactor system is batch or continuous or a hybrid such as semi-batch, wherein the reactor residence time distribution is narrow such as in non-backmixed reactors or broad such as in backmixed reactor and series and recycle reactors.

BRIEF DESCRIPTION OF FIGURES

[0008] FIG. 1 is a graphical depiction of the molecular weight of a polymer as the number of branching methines per 1000 carbons increase.

[0009] FIG. 2 is a graphical model predicted dependence of molecular weight distribution (MWD) curve on branching level.

[0010] FIG. 3 is a graphical model predicted dependence of relative peak molecular weight on branching level.

[0011] FIG. 4 is a graphical depiction of a predicted dependence of the molecular weight distribution (MWD) curve on tri-functional dienes branching level.

[0012] FIG. 5 is a graphical depiction of a predicted dependence of relative peak of the molecular weight (MW) on tri-functional dienes branching level.

[0013] FIG. 6 is a graphical depiction of a model-predicted effect of branching on peak molecular weight (M_p) versus branches per polymer molecule of conventional diene branching (solid line) and "Ladder branching" (dashed line).

[0014] FIG. 7 is a graphical depiction of a model-predicted effect of branching on weight average molecular weight (M_w) versus branches per polymer molecule of conventional diene branching (solid line) and "Ladder Branching" (dashed line).

[0015] FIG. 8 is a graphical depiction of a model-predicted effect of branching on peak weight average molecular weights (M_p) versus branches per linear chain segment of conventional diene branching (solid line) (vs. B_c) and the M_p of "Ladder Branched" polymers (dashed line) (vs. R_c).

[0016] FIG. 9 is a graphical depiction of a model-predicted effect of branching weight average molecular weight (M_w) versus branches per linear chain segment for conventional diene branching (vs. B_c) (solid line) and "Ladder Branched" polymer (dashed line) (vs. R_c).

[0017] FIG. 10 is a graphical depiction of MWD slopes used to calculate shape metrics G(79/29) and G(96/08) where S(X) is the slope at X% of the MWD height. G(A/B) = (S(A) - S(B)) / S(A).

[0018] FIG. 11 is a graphical depiction of a model predicted molecular weight distribution (MWD) shape metric G(79/29) compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative peak MW(M_p/M_{po}).

[0019] FIG. 12 is a graphical depiction of a model predicted MWD shape metric G(79/29) compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative weight average MW (M_w/M_{wo}).

[0020] FIG. 13 is a graphical depiction of a model predicted MWD shape metric G(98/08) compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative peak MW (M_p/M_{po}).

[0021] FIG. 14 is a graphical depiction of a model predicted MWD shape metric G(98/08) compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative weight average MW (M_w/M_{wo}).

[0022] FIG. 15 is a graphical depiction of the MWD curve illustrating how the high MWD tail area metrics are defined using the point of maximum slope.

[0023] FIG. 16 is a model predicted MWD area metric, $A_{HIGH,}$ compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative weight average molecular weight (M_p/M_{po}).

[0024] FIG. 17 is a model predicted MWD area metric, $A_{HIGH,}$ compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative peak molecular weight (M_w/M_{wo}).

[0025] FIG. 18 is a model predicted MWD area metric, $A_{TAIL,}$ compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative peak molecular weight (M_p/M_{po}).

[0026] FIG. 19 is a model predicted MWD area metric, $A_{TAIL,}$ compared for conventional and "Ladder Branching" as a function of branching level as depicted by relative weight average molecular weight (M_w/M_{wo}).

[0027] FIG. 20 is a graph of the absolute molecular weight distribution (MWD) curve as measured by GPC for Example Series 2.4 as recorded in Table 2.

[0028] FIG. 21 is a conventional molecular weight distribution curve measured by conventional gel permeation chromatography (GPC).

[0029] FIG. 22 is an absolute molecular weight distribution curve measured by GPC triple light scattering detector (also called Absolute GPC).

[0030] FIG. 23 is a graph of the extensional viscosity as measured as a function of time in seconds for a "Ladder Branched" polymer resin.

[0031] FIG. 24 is a graph of the melt strength (cN) as a function of velocity (mm/s) for a "Ladder Branched" polymer resins.

[0032] FIG. 25 is a conventional molecular weight distribution curve measured by GPC of an unbranched ethylene-based polymer and a "Ladder Branched" polymer resin.

[0033] FIG. 26 is an absolute molecular weight distribution curve measure by a GPC triple light scattering detector of an unbranched ethylene-based polymer and a "Ladder Branched" polymer resin.

[0034] FIG. 27 is a graph of the extensional viscosity as measured as a function of time in seconds of a "Ladder Branched" polymer resin.

[0035] FIG. 28 is a graph of the melt strength (cN) as a function of velocity (mm/s) of a "Ladder Branched" polymer resin.

[0036] FIG. 29 is an absolute molecular weight distribution curve measured by a GPC triple light scattering detector for two comparative examples having no diene and four samples having a variable amount of diene.

[0037] FIG. 30A is a graph of the absolute molecular weight distributions of comparative conventional branched polymer samples with varying amounts of diene.

[0038] FIG. 30B is a graph of the conventional molecular weight distributions of comparative conventional branched polymer samples with varying amounts of diene.

[0039] FIG. 31 is a graph of the rheology ratio as a function of average g' for various polymer resins and "Ladder Branched" polymer resins.

[0040] FIG. 32 is a graph of the rheology ratio as a function of polydispersity index (PDI) for various polymer resins and "Ladder Branched" polymer resins.

[0041] FIG. 33 is a graph of the melt strength (centiNewtons, cN) as a function of the melt index (Log I_2) of polymers produced with a single chain catalyst and a dual chain catalyst, with

additional lines depicting linear polyethylene, tubular low density polyethylene and autoclave low density polyethylene.

DETAILED DESCRIPTION

[0042] Specific embodiments of a process for synthesizing polymer and polymers synthesized by the process of this disclosure will now be described. It should be understood that the process for synthesizing polymers of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

[0043] DEFINITIONS

[0044] 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 monomers. The term "interpolymer," as used herein, refers to a polymer prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers, and polymers prepared from more than two different types of monomers, such as terpolymers.

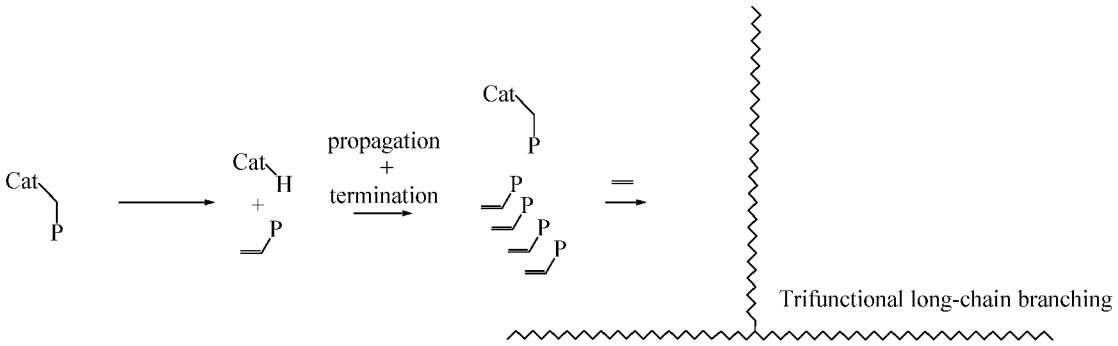
[0045] "Polyethylene" or "ethylene-based polymer" shall mean polymers comprising greater than 50% by weight of units which have been derived from ethylene monomer. This includes polyethylene homopolymers or copolymers (meaning units derived from two or more comonomers). Common forms of polyethylene known 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).

[0046] Embodiments of this disclosure include a process of synthesizing long-chain branched polymers by adding a C_2 monomer, optionally at least one or more C_3-C_{12} α-olefin comonomer, at least one diene, a multi-chain catalyst, and optionally, a solvent, in which the

multi-chain catalyst includes a molecule having a plurality of polymerization sites, producing at least two copolymer strands, each copolymer strand copolymerizing at one of the polymerization sites; and synthesizing the long-chain branched polymers by connecting the two copolymer strands with the diene, the connection of the two copolymer strands being performed concertedly with the copolymerization.

[0047] The process of synthesizing polymers according to this disclosure is different from the conventional long-chain branching. The term "long-chain branching" refers to branches having greater than 100 carbon atoms. A "branch" refers to a portion of polymer that extends from a tertiary or quaternary carbon atom. When the branch extends from a tertiary carbon atom, there are two other branches, which collectively could be the polymer strand from which the branch extends. Conventionally, long-chain branching (LCB) may occur naturally in the polymerization process, as shown in Scheme 1. This can occur through vinyl termination of the polymer chain and reinsertion of the macromolecular vinyl creating a tri-functional long-chain branch. Depending on the degree of branching, a variety of methods can either determine LCB, such as nuclear magnetic resonance (NMR), or distinguish the effect of LCB in the polymer. For example, the effect of LCB is observed in shear flow in the van Gurp-Palmen analysis, also an increase of the shear viscosity at low angular frequencies and strength of the shear thinning behavior can be attributed to LCB. In extensional flow, the influence of LCB is usually identified in the degree of hardening or the strength of the melt and the maximum deformation achieved. A high level of natural LCB in a polymer is difficult to achieve due to the limited concentration of vinyl terminated polymers (maximum one per polymer chain) and the need to run to high ethylene conversion to ensure LCB formation. To ensure high conversion, there is a low ethylene concentration in the reactor, thus enabling a great amount of vinyl terminated polymers to be reinserted in a second polymer chain.

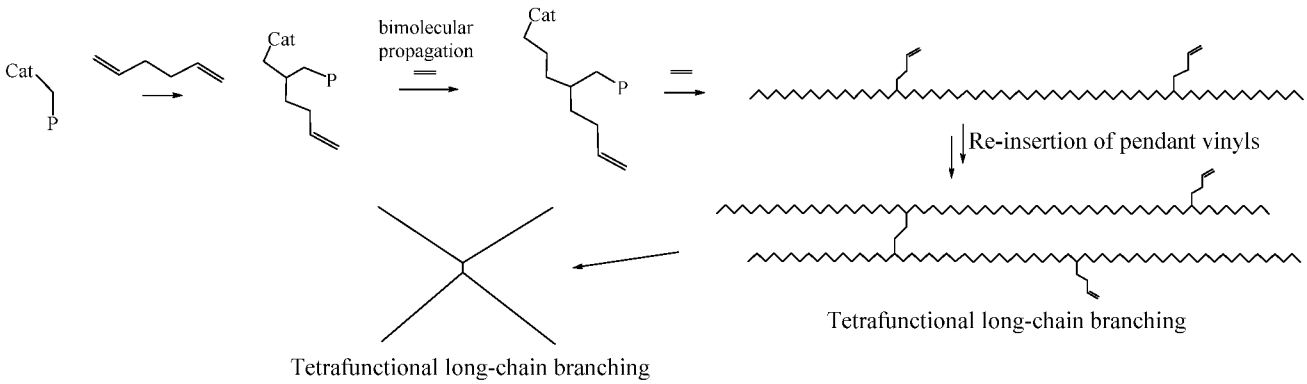
Scheme 1: Naturally occurring long-chain branching: Chain transfer event leading to vinyl terminated polymers



[0048] In Scheme 1, "Cat" is the catalyst and "P" is the polymer chain.

[0049] There is minimal long-chain branching that forms through the naturally occurring branching process. One way to enhance LCB is through the addition of α,ω-dienes to the polymerization system, whether it be in a radical, heterogeneous, or homogeneous process. In general, dienes add to the polymer chain in a similar manner to α-olefins, but leave a pendant vinyl group which can insert into a polymer chain a second time to create the LCB, as illustrated by Scheme 2. In general, the diene length does not matter, only that it can link two polymer chains together. In principle, the concentration of pendant vinyls can be controlled through the amount of diene added to the reactor. Thus, the degree of LCB can be controlled by the concentration of pendant vinyls.

Scheme 2: Long-Chain Branching via Diene Incorporation



In Scheme 2, "Cat" is the catalyst; "P" is the polymer chain; and the diene in this example is 1,5-hexadiene.

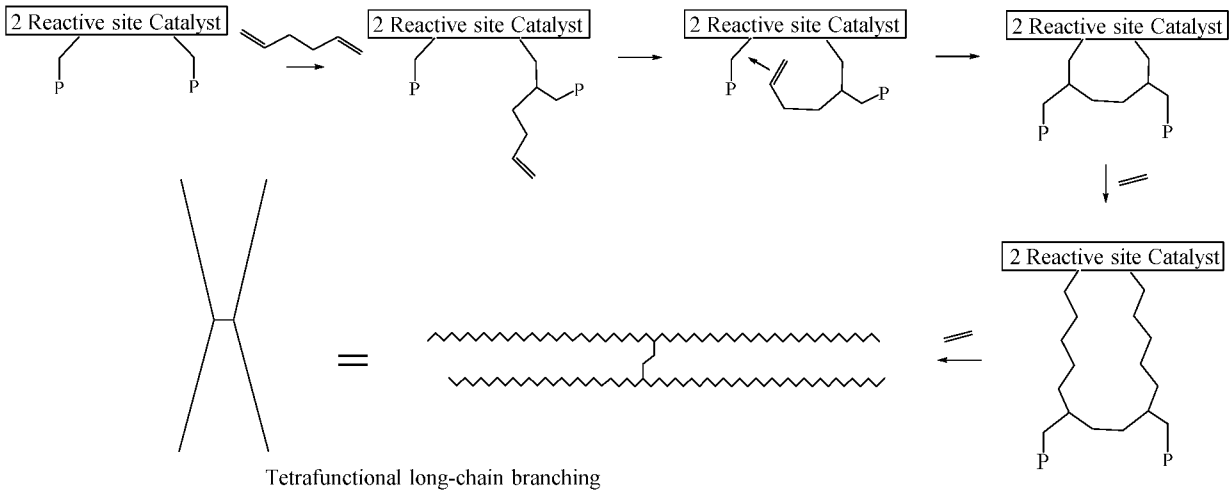
[0050] The conventional process of incorporating dienes into a polymer synthesis system suffers from the fundamental flaw of gel formation or reactor fouling. The kinetic modeling, discussed in later paragraphs, may provide good predictive results that enable a better understanding into gel formation. For example, longer polymer chains have more inserted olefins, thus more inserted dienes, thus more pendant vinyls, implying that longer polymer chains will be more likely to re-insert into the catalyst to form a LCB. Thus, the longer polymer chains preferentially re-insert forming tetra-functional branches, which are even larger polymer molecules, and a gel problem results. As indicated in Scheme 2, a tetra-functional LCB has a short segment (number of carbons between the two double bonds of the diene), which bridges two long chains on each side of the short segment. A simulation of the weight average molecular weight (M_w) and number average molecular weight (M_n) as a function of branching is shown in FIG. 1 for polyethylene in a semi-batch reactor at constant pressure. In FIG. 1, M_n only marginally increases as M_w becomes infinite. As the M_w increases to a number greater than 200,000 grams per mole (g/mol), the polymer gels, gelling occurs, or reactor fouling is present.

[0051] The term "gel" or "gelling" refers to a solid composed of at least two components: the first is a three dimensional cross-linked polymer and the second is a medium in which the polymer does not fully dissolve. When the polymer gels and does not fully dissolve, the reactor may become fouled with polymer gel.

[0052] The term "Ladder Branched" polymer refers to the tetra-functional long chain branched polymer as disclosed in this application, and the term or "Ladder Branching mechanism" refers to how the "Ladder Branched" polymers are formed.

[0053] In one or more embodiments of this disclosure, the process to synthesize the long-chain branched polymer achieves long-chain branching and avoids gel formation or reactor fouling. Without intending to be bound by theory, it is believed that reactor fouling is avoided by reacting the two alkenes of the diene in a concerted fashion across two proximal polymer chains. For example and illustrated by Scheme 3, one alkene of the diene reacts before the second alkene, and the second alkene reacts before too many ethylene molecules are added to the polymer strand, thereby removing the close proximity the second alkene has to the reactive site. The reaction of the first alkene of the diene into one polymer and second alkene of the diene into an adjacent polymer chain before many ethylene monomers are inserted is referred to as a concerted addition of the diene into proximal polymer chains.

Scheme 3: Depiction of incorporating the diene in a concerted fashion (P is a polymer chain), also called the "Ladder Branching" mechanism.



[0054] Polymer strands are linear segments of a polymer, or more specifically a copolymer, which are optionally joined at the end(s) by branching junctures. For example, a tetra-functional branch juncture joins the ends of four polymer strands, as opposed to a tri-functional branch juncture, which joins the ends of three polymer strands as shown in Scheme 1.

[0055] The combination of a multi-chain catalyst and diene influences the amount and type of branching. Embodiments of the present disclosure are directed to controlling polymer properties such as: 1) the use of multiple diene species, 2) the use of multiple multi-chain catalyst species, or 3) the combination of polymerization environments including multiple reactors zones or a gradient of zones.

[0056] Although, using multiple catalysts, including single-chain catalysts, may allow conventional branching. The use of multiple dienes species also includes those dienes which do not create branches or tend to result in "conventional" LCB. The process of synthesizing polymers according to this disclosure is different from the conventional long-chain branching. The term "long-chain branching" refers to branches having greater than 100 carbon atoms. The term "branch" refers to a portion of polymer that extends from a tertiary or quaternary carbon atom. When the branch extends from a tertiary carbon atom, there are two other branches, which collectively could be the polymer chain from which the branch extends. Long-chain branching (LCB) may occur naturally in the polymerization process, as shown in Scheme 1. This may occur through termination of the polymer chain and reinsertion of the macromolecular vinyl creating a tri-functional long-chain branch.

[0057] In one or more embodiments, the process for polymerizing the long-chain branched polymer includes a catalyst with at least two active sites in close proximity (multi-chain catalysts). In order for the two active sites to be in close proximity, the two active sites may be less than 18.5 angstroms (Å) apart. In some embodiments, the two active sites include a distance of from 2.5 angstroms (Å) to 18.5 Å, from 9 Å to 14 Å, or approximately 11 Å. In various embodiments, the process for polymerizing the long-chain branched polymer includes a multi-chain catalyst. In one or more embodiments, the multi-chain catalyst may include at least one metal center, in which the two active site are on the same metal center. In some embodiments, the multi-chain catalyst may include a metal–ligand complex, in which the two active sites (two polymer chains) are on the same metal center.

[0058] According to an X-ray crystal structure (A.D. Bond, *Chem. Comm.* **2002**, 1664), 1,9-decadiene has a distance between terminal carbons of 10.8 Å. While there is data that the 1,9-decadiene form rungs between two polymer chains via the "Ladder Branching" mechanism, one may believe that α,ω-dienes having more than 10 carbon atoms may also form rungs via the "Ladder Branching" mechanism. Without intent to be bound by theory, the issue of whether α,ω-dienes having more than 10 carbon atoms may form rungs may be determined by the distance between the two polymer chains. For example, when the two polymer chains reside on different metal atoms of a catalyst (e.g., bimetallic, heterogeneous), the α,ω-dienes may include additional methylene units (same C-C bond lengths and angles) to extend this structure to 1,15-hexadecadiene. Without intent to be bound by theory, it is presumed this 16-carbon analog still has the potential to form a rung via the "Ladder Branching" mechanism. In this manner, one can consider dienes, 1,11-dodecadiene (13.3 Å distance between terminal carbons), 1,13-tetradecadiene (15.9 Å distance between terminal carbons), 1,15-hexadecadiene (18.5 Å distance between terminal carbons). In some embodiments, when the dual chain catalyst in the "Ladder Branching" mechanism is a bimetallic catalysts, the diene is less than or equal to 18.5 Å.

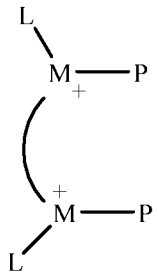
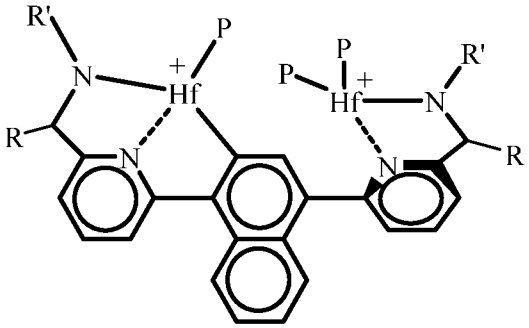
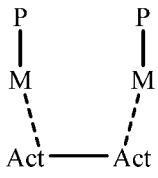
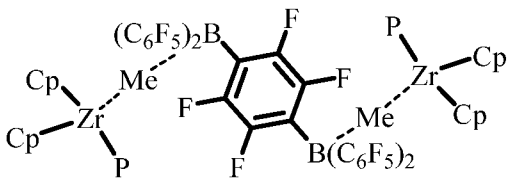
[0059] It is well-known that modern computational techniques can reproduce known experimental crystal structures to high accuracy as a way to estimate distances between chains for a catalyst. For a heterogeneous system, one may estimate surface concentration of metals which are often measured in metal atoms per nanometer squared (M/nm^2). This surface coverage provides an estimate of accessible metals on the surface which if evenly dispersed may be converted to an M-M distance, which reflects the distance between the polymer chains. For an

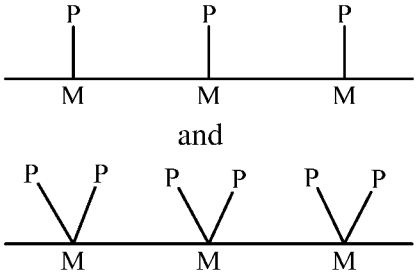
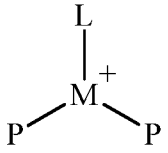
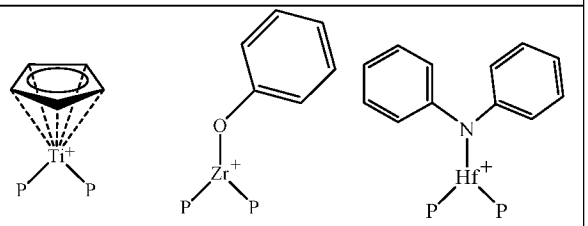
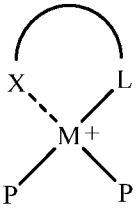
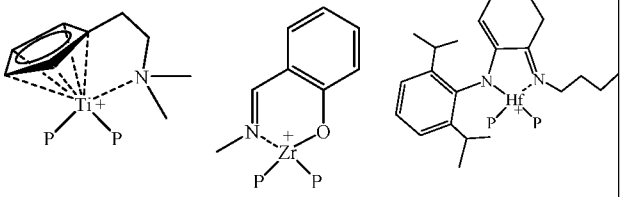
extended surface, 1 metal/nm^2 leads to a distance of 10 Å between the metal atoms, well within the desired cut-off. At 18.5 Å, one can determine the coverage at 0.3 metal/nm^2.

[0060] Examples of catalysts having at least two active sites, wherein the active sites are in close proximity include, but are not limited to, bimetallic transition metal catalysts; heterogeneous catalysts; dianionic activators with two associated active catalysts; a ligated transition metal catalyst with more than one propagating polymer chain; a group IV olefin polymerization catalyst including monoanionic groups, bidentate monoanionic groups, tridentate monoanionic groups, or a monodentate, bidentate, or tridentate monoanionic groups with external donors.

[0061] The catalysts in Table 1 are illustrative embodiments of the classes of catalysts previously described and specific catalysts contemplated. The examples in Table 1 are not intended to be limiting; rather they are merely illustrative and specific examples for the classes of catalyst previously mentioned.

Table 1: Catalysts with more than one active site in close proximity

Class	Illustrative	Specific
Bimetallic Catalysts		
	 Dianionic Activator associated with two active catalyst	

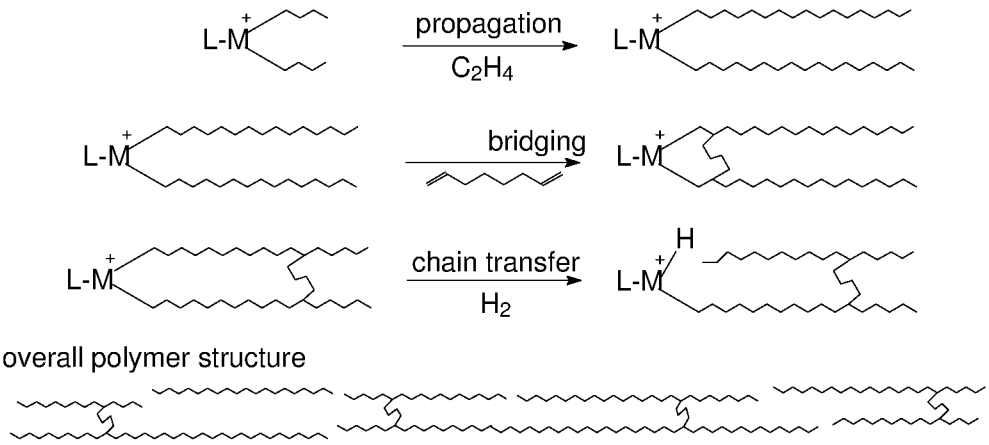
Heterogeneous and Supported Catalysts	 and Heterogeneous Catalyst
Group IV Olefin Polymerization Catalyst	 M=Ti,Zr,Hf Monoanionic groups    Bidentate monoanionic groups

[0062] While not intending to be bound by theory, a mechanism, as explained in this section, describes how a dual chain catalyst can create a unique bridged molecular architecture when polymerizing diene co-monomers under desired conditions. The term "diene" refers to a monomer or molecule having two alkenes. A pictorial description of the kinetics is shown in Scheme 4, in which the catalyst center produces two polyolefin chains. Scheme 4 shows how a combination of diene bridging and chain transfer may create a diene "Ladder Branched" polymer structure. The term diene "Ladder Branched" polymer refers to the long-chain branching, in which a short chain or rung that includes one to twelve carbon atoms links two long-chains together. As shown, the metal-ligand catalyst having at least two polymer chain sites propagates two separate polymer chains. One alkene of the diene is incorporated into one of the sites of the catalyst, and it is believed that due to the close proximity of the propagation sites, the second alkene of the diene is then quickly incorporated into the second polymer chain, thereby forming a bridge or rung. This successive addition of diene is referred to as a "concerted" addition of the diene, distinguishing it from catalysts without two proximal chains where diene addition leads to a concentration of vinyl containing polymers in the reactor, which react at a later time. The term "rung" refers to the diene once it is incorporated into two separate polymer

strands, thereby linking the strands together. The first and second polymer strands continue to propagate until the polymer transfers to another catalyst, the polymer is released from the catalyst, the catalyst dies, or another diene is added.

Kinetics

Scheme 4. Illustration of "Ladder Branching" kinetics including the resulting molecular architecture. The metal–ligand catalyst are represented together by L-M^+.



[0063] Without intending to be bound by theory, it is believed that the molecular weight distribution associated with these proposed kinetics is inherently stable at high branching levels when the diene bridging reaction is the sole source of branching. The molecular weight distribution (MWD) is defined by the weight average molecular weight divided by the number average molecular weight (M_w/M_n). The inherent stability of the MWD means that the weight average molecular weight (M_w) increases only moderately even at high branching levels, which is in contrast to conventional diene comonomer branching technology wherein M_w and M_w/M_n become infinite at moderate tetra-functional branching levels.

[0064] A mathematical model is derived for the purpose of demonstrating how the process for synthesizing polyethylene creates a long-chain branched polymer having a diene "Ladder Branched" molecular architecture. The mathematical model will also be used to establish claims metrics and ranges. The mathematical model of the branched architecture as described in this disclosure may be derived from a kinetics description of the proposed mechanism of branching. This model is based upon several assumptions to facilitate mathematical simplicity, but these assumptions are not intended to limit the scope of this disclosure. The assumptions follow common industrial applications of non-living addition of copolymers as well as additional

assumptions specific to the assumed diene branching mechanism. The common assumptions made include: (1) propagation is much faster than chain transfer, therefore average chain length is much greater than one monomer; (2) only a single pure catalyst species is active; (3) the catalyst center makes many chains during its lifetime, and therefore the chain lifetime is a small fraction of the reaction or residence time; (4) co-polymerization may be approximated by a homopolymerization model when there is negligible composition drift.

Kinetics for Diene "Ladder Branching" Theory

[0065] In addition to the four commonly made assumptions, there are four assumptions, on which the kinetics for diene "Ladder Branching" theory is based. The first assumption is that the catalyst center simultaneously produces two kinetic chains with identical kinetics and statistics. Secondly, the rung is formed when a diene bridges two polymer chains increasing in length. Third, the branch point is formed whenever two un-bridged chains are bridged by a diene. Finally, the diene reactions not forming bridges are ignored since the MWD is not affected.

[0066] The kinetic description of a proposed diene "Ladder Branching" mechanism requires the deployment of a nomenclature that describes how each reaction affects the molecular architecture. Some nomenclature elements below represent small molecules (M, A, D) while the other nomenclature elements represent the molecular architecture ($P_{n,m}$, S_n, D_n). The kinetics will show how the nomenclature elements interact to form the molecular architecture.

Kinetic Nomenclature

[0067] **M** : monomer or co-monomers; **A** : chain transfer agent species; **D** : diene branching species; **n, m** : indices reflecting the number of monomeric repeat units on a subspecies; $\mathbf{P_{n,m}}$: catalyst with two un-bridged propagating polymers having n and m monomeric repeat units; $\mathbf{D_n}$: dead polymer molecular with n monomeric repeat units; $\mathbf{S_n}$: catalyst producing a bridged polymer molecule with n monomeric repeat units; **Kc** : kinetic chains are defined as linear segments created by chain transfer; **Rg** : rungs are defined as bridges between chain segments; **Br** : branches are created when two previously un-bridged molecules become bridged.

[0068] The equations for branching kinetics are written below using the nomenclature and assumptions introduced above. A brief description will be given for each reaction, and anyone

skilled in the art of polymerization kinetics should be capable of comprehending the kinetic scheme and rate laws.

Table 2: Kinetics for Diene "Ladder Branching" Theory, **(n≥1, m ≥1)**

	Chain position	Reaction	Reaction Constant
Propagation	(left)	$P_{n,m} + M \rightarrow P_{n+1,m}$	k_p, (L/mole/sec)
	(right)	$P_{n,m} + M \rightarrow P_{n,m+1}$	k_p, (L/mole/sec)
		$S_n + M \rightarrow S_{n+1}$	2 k_p, (L/mole/sec)
Chain Transfer	(left)	$P_{n,m} + A \rightarrow P_{0,m} + D_n + kc$	k_{tra}, (L/mole/sec)
	(right)	$P_{n,m} + A \rightarrow P_{n,0} + D_m + kc$	k_{tra}, (L/mole/sec)
	(right)	$P_{n,m} + A \rightarrow P_{n,0} + D_m + kc$	k_{tra}, (L/mole/sec)
	(left)	$S_n + A \rightarrow P_{0,n} + kc$	k_{tra}, (L/mole/sec)
	(right)	$S_n + A \rightarrow P_{n,0} + kc$	k_{tra}, (L/mole/sec)
Diene Bridging		$P_{n,m} + D \rightarrow S_{n+m} + br + rg$	4 k_d, (L/mole/sec)
		$S_n + D \rightarrow S_n + rg$	4 k_d, (L/mole/sec)
Re-initiation		$P_{n,0} + M \rightarrow P_{n,1}$	fast reaction
		$P_{0,m} + M \rightarrow P_{1,m}$	fast reaction

[0069] The outcome of propagation is the incremental increase in chain size by one repeat unit. Propagation is written separately for each of the two molecules increasing in length from a catalyst center. For example, the first index on $P_{n,m}$ is for the left chain on the catalyst and the second index is for the right chain on the catalyst. When propagation is modeled for an increase in length bridged molecule (S_n), a factor of 2 appears in the rate, because there are two chain positions, the left and the right, on each center equally available for reaction.

[0070] Chain transfer, like propagation, is written separately for the left and right positions on the catalyst. Chain transfer of an un-bridged species ($P_{n,m}$) produces a dead polymer molecule (D_n or D_m) and a vacant position ($P_{0,m}$ or $P_{n,0}$). When a propagating bridged molecule (S_n) engages in chain transfer, an un-bridged species ($P_{n,0}$ or $P_{0,n}$) is produced and no dead polymer is produced since all n repeat units are still bonded to the catalyst. The vacant positions ($P_{0,m}$ and

$P_{n,0}$) resulting from chain transfer are assumed to very quickly re-initiate and engage in propagation. The rate expressions for diene bridging include a factor of 4 because each diene has two polymerizable groups and each catalyst center has two positions (left and right) for diene incorporation.

[0071] Diene bridging results in the formation of a tetra-functional branch (br) only when un-bridged ($P_{n,m}$) species react productively with a diene. A tetra-functional branch refers to a short segment where four polymer chains can emanate from, two from each side of the short segment. With dienes, tetra-functional branches are the expected type of LCB. A rung is produced (rg) when any catalyst center productively incorporates a diene regardless of whether it has bridged (S_n) or un-bridged ($P_{n,m}$) molecules. Diene reactions that do not result in bridging, such as intra-chain cyclization and pendant vinyl formation, are ignored and are considered non-productive for these kinetics.

[0072] The creation of a model from the kinetics requires that a series of population balances be derived for each type of polymer species involved. These population balances are derived as a function of chain length (n, m) and represent kinetic rates of change of the various polymeric subspecies. The population balances are given below assuming mass action rate laws with $P_{n,m}$, S_n, and D_n symbols representing the molar concentration of subspecies for $n \geq 1$ and $m \geq 1$. The kinetics model can be extended to include other chain transfer reactions, such as with hydrogen (k_{trh}) and beta hydride elimination (k_b) merely by expanding the definition of the transfer term, $\Omega = k_{tra}A + k_{trh}H_2 + k_b$.

$$R_{S_n} = 2\Psi \sum_{m=1}^{n-1} (P_{m,n-m} + P_{n-m,m}) + 2\Phi (S_{n-1} - S_n) - 2\Omega S_n \quad (1)$$

$$R_{P_{n,m}} = \Phi (P_{n-1,m} + P_{n,m-1} - 2P_{n,m}) - (2\Omega + 4\Psi)P_{n,m} + \delta_{m-1}\Omega(S_n + L_n) + \delta_{n-1}\Omega(S_m + R_m) \quad (2)$$

$$R_{D_n} = \Omega \sum_{s=1}^{\infty} (P_{s,n} + P_{n,s}) = \Omega (R_n + L_n) \quad (3)$$

[0073] In equations (1), (2), and (3):

$$\Omega = k_{tra} A \quad (4)$$

$$\Psi = k_d D \quad (5)$$

$$\Phi = k_p M \quad (6)$$

$$L_n = \sum_{s=1}^{\infty} P_{n,s} \quad (7)$$

$$R_n = \sum_{s=1}^{\infty} P_{s,n} \qquad \delta_i = \begin{cases} 0, & i \neq 0 \\ 1, & i = 0 \end{cases} \tag{8}$$

[0074] Other important population balances may be derived from equations (1) to (8), such as the propagating polymer subspecies distributions for the left side (L_n) and right side (R_n). The left and right side distributions of the propagating polymer subspecies are equal, due to symmetry imposed in defining the kinetics scheme.

$$R_{L_n} = \Phi\,(L_{n-1} - L_n) - (\Omega + 4\Psi)L_n + \Omega\, S_n + \delta_{n-1}\Omega(\xi_{0,0} + \mu_0) \tag{9}$$

$$R_{R_n} = \Phi\,(R_{n-1} - R_n) - (\Omega + 4\Psi)R_n + \Omega\, S_n + \delta_{n-1}\Omega(\xi_{0,0} + \mu_0) \tag{10}$$

[0075] The rates of formation of molecular attributes such as kinetic chains (kc), branches (br), and rungs (rg) are expressed below using mass action rate laws derived from the kinetics scheme. A shorthand notation is used to define the concentration of catalyst with un-bridged molecules ($\xi_{0,0}$) and the concentration of catalyst with bridged polymer molecules (μ_0). Therefore the total catalyst concentration is $\xi_{0,0}+\mu_0$.

$$R_{kc} = 2\,\Omega \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} P_{n,m} + 2\,\Omega \sum_{n=1}^{\infty} S_n = 2\,\Omega\,(\xi_{0,0} + \mu_0) \tag{11}$$

$$R_{br} = 4\,\Psi \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} P_{n,m} = 4\,\Psi\,\xi_{0,0} \tag{12}$$

$$R_{rg} = 4\,\Psi \sum_{n=1}^{\infty}\sum_{n=1}^{\infty} Pn,m + 4\,\Psi \sum_{n=1}^{\infty} Sn = 4\,\Psi\,(\xi_{0,0} + \mu_0) \tag{13}$$

$$\xi_{0,0} = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} P_{n,m} = \sum_{n=1}^{\infty} R_n = \sum_{n=1}^{\infty} L_n \tag{14}$$

$$\mu_0 = \sum_{n=1}^{\infty} Sn \tag{15}$$

[0076] The first step in rendering a usable model is to implement the "steady-state assumption" on the distributions of the propagating polymer species by setting the relevant polymer subspecies rates ($R_{P_{n,m}}$, R_{S_n}, R_{L_n}, R_{R_n}) to zero. This is a very common assumption in addition polymerization modeling when the lifetime of propagating chain is a very small fraction of the time period of interest. In most non-living commercial polymerizations of this type, the chain lifetime is typically much less than a second while a reactor residence time is at least

several minutes. The following relation is derived after implementing the "steady-state" assumption and summing the live rates over all indices.

$$2\Psi\ \xi_{0,0} = \Omega\ \mu_0, \quad \text{therefore } \xi_{0,0} = \frac{\Omega}{\Omega+2\Psi}\ (\xi_{0,0} + \mu_0) \tag{16}$$

[0077] The "steady-state assumption" results in relations for simple branching metrics (B_c, B_n, R_c) that will be useful in the molecular architecture model. In this particular case, instantaneous properties are convenient and relevant because they apply to a variety of reactors such as a steady state, well-mixed reactor or a batch reactor with negligible drift in temperature or composition. The instantaneous branching metrics (B_c, B_n, R_c) are equivalent to their cumulative average values when there is no spatial or temporal variation in chain transfer (Ω) and diene bridging rate (Ψ) parameters.

$$\text{Instantaneous Tetra-Functional Branches per Kinetic Chain, } B_c = \frac{R_{br}}{R_{kc}} = \frac{2\Psi}{\Omega+2\Psi} \tag{17}$$

$$\text{Instantaneous Tetra-Functional Branches per Polymer Molecule, } B_n = \frac{R_{br}}{R_{\lambda_0}} = \frac{2\Psi}{\Omega} \tag{18}$$

$$\text{Instantaneous Rungs per Kinetic Chain, } R_c = \frac{R_{rg}}{R_{kc}} = \frac{2\Psi}{\Omega} \tag{19}$$

Moments for Prediction of MWD Averages

[0078] A model describing the moments of the polymer species chain length distributions can often be derived from population balances resulting from a kinetics scheme. A moment based model is useful in predicting molecular weight averages and polydispersity index but in general does not describe smaller nuances in MWD such as bimodality, peak MW, and tailing. The method of moments entails the definition of various polymeric subspecies chain length distribution moments such as those below. The bulk polymer moments (λ_i) reflect bulk polymer properties and solution of a model of bulk moments generally requires solution of various living polymer moments.

$$\text{Living Polymer MWD Moments:} \quad \mu_i = \sum_{n=1}^{\infty} n^i\ S_n \qquad \xi_{i,j} = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} n^i\ m^j\ P_{n,m} \tag{20}$$

$$\text{Bulk Polymer MWD Moments:} \quad \lambda_i = \sum_{n=1}^{\infty} n^i\ (D_n + S_n + L_n + R_n) \approx \sum_{n=1}^{\infty} n^i\ D_n \tag{21}$$

[0079] Any skilled polymer reaction engineer would understand the derivations of a Moments Model (Equations (20) and (21)) from a series of population balances. Rates of change of the leading bulk polymer moments (λ_0, λ_1, λ_2) are given below with negligible terms removed after imposing the assumption that kinetic chains are long, and therefore $\Phi >> \Omega$.

$$R_{\lambda_0} = 2\Omega(\mu_0+\xi_{0,0}) - 4\Psi\xi_{0,0} \qquad R_{\lambda_1} = 2\Phi(\mu_0+\xi_{0,0}) \qquad R_{\lambda_2} = 2\Phi(\xi_{1,0}+\xi_{0,1}+2\mu_1) + 8\Psi\xi_{1,1} \tag{22}$$

[0080] Evaluation of the rates of change of these bulk moments requires a number of living polymer subspecies moments. These live polymer moments are algebraic quantities because of the "steady-state assumption" and are given below. Additional live moments are required when higher bulk moments such as λ_3 are predicted.

$$\xi_{0,0}=\frac{\Omega\,\mu_0}{2\Psi} \qquad \xi_{1,0}=\xi_{0,1}=\frac{\Phi\xi_{0,0}+\Omega\mu_1}{\Omega+4\Psi} \qquad \xi_{1,1}=\frac{\Phi(\xi_{1,0}+\xi_{0,1})}{2\Omega+4\Psi} \qquad \mu_1=\frac{\Phi\mu_0+2\Psi(\xi_{1,0}+\xi_{0,1})}{\Omega} \tag{23}$$

[0081] The instantaneous number and weight average chain lengths (DPn, DPw) are provided below, after algebraic simplification of the moment rates. Of course, the average molecular weights (M_n, M_w) are equal to the average chain lengths multiplied by the apparent monomeric repeat unit weight in g/mole.

$$DP_n = \frac{R_{\lambda_1}}{R_{\lambda_0}} = \frac{\Phi(2\Psi+\Omega)}{\Omega^2} \qquad Z_p = \frac{DP_w}{DP_n} = \frac{R_{\lambda_2} R_{\lambda_0}}{(R_{\lambda_1})^2} = \frac{2(8\Psi^2 + 10\Psi\Omega + \Omega^2)}{(2\Psi + \Omega)^2} \tag{24}$$

[0082] The expression of the model is further simplified by a few substitutions, such as the average linear kinetic chain length DP_{no} being equal to Φ/Ω. Also, the model can be expressed as a function of any of the instantaneous branching metrics B_c, B_n, and R_c. The model is written below in terms of diene "Ladder Branches" per kinetic chain (B_c) and branches per polymer molecule (B_n). It was previously shown that branches per polymer molecule equals rungs per kinetic chain ($B_n=R_c$) for this system.

$$DP_n = \frac{DP_{no}}{1 - B_c} = DP_{no}\,(1+B_n) \tag{25}$$

$$Z_p = \frac{DP_w}{DP_n} = \frac{M_w}{M_n} = 2 + 6\,B_c - 4\,B_c^2 = \frac{2 + 10\,B_n + 4\,B_n^2}{(1+B_n)^2} \tag{26}$$

[0083] The number and weight average molecular weights (M_n, M_w) can also be predicted as functions of diene "Ladder Branches" per kinetic chain (B_c) or branches per polymer molecule (B_n) after defining the number and weight average linear kinetic chain weight as M_{no} and M_{wo}.

$$M_n = \frac{M_{no}}{1 - B_c} = M_{no}(1+B_n) \tag{27}$$

$$M_w = M_{wo}\frac{2 + 6\,B_c - 4\,B_c^2}{1 - B_c} = M_{wo}\frac{2 + 10\,B_n + 4\,B_n^2}{1+B_n} \qquad \text{where} \quad M_{wo} = 2\,M_{no} \tag{28}$$

[0084] An unexpected prediction arising from the Moments Model (Equations (20) and (21)) is that at high dienes branching levels, the maximum polydispersity is about 4. Of course, this prediction is for an ideal co-polymerization and a single symmetric catalyst system and any non-idealities are likely to give an increased polydispersity.

Model of the Complete MWD Curve

[0085] At times, it is possible to solve population balances for a molecular weight distribution curve. Explicit algebraic solutions are normally only available for instances of no spatial or temporal variations in reaction rates, such as assumed in this case. The solution begins with the definition of yet another distributional quantity Vn derived from Pn,m. The population balance for Vn is derived by summing over the population balance for Pn,m, with simplification due to symmetry.

$$V_n = \sum_{m=1}^{n-1} P_{m,n-m} = \sum_{m=1}^{n-1} P_{n-m,m} \tag{29}$$

$$R_{V_n} = 0 = 2\Phi\,(V_{n-1} - V_n) - (2\Omega+4\Psi)V_n + 2\,\Omega(S_n + L_n) \tag{30}$$

[0086] Due to the assumption of long chains, it is possible to treat all subspecies distributions as if they were continuous rather than discrete functions. The discrete steady-state polymer species population balances can be closely approximated by differential equations in the continuous variable n when difference terms are replaced by derivatives. For example, the steady-state population balance for Sn contains the difference term Sn–Sn-1 which is replaced by the derivative as shown in equation (31).

$$\Phi(S_n - S_{n-1}) \sim \Phi\frac{dS(n)}{dn} \tag{31}$$

[0087] Similar replacements result in the following series of ordinary differential equations (ODEs) which can be integrated to yield the chain length distributions of the various defined live subspecies distributions L(n), S(n), and V(n). The model is summarized below as an initial value problem, where the chain length distribution functions are assumed to start at n=0. The lower

limit of n=0 for the distribution functions is chosen for mathematical simplicity alone and ultimately makes no significant impact on model predictions when high polymers are formed.

$$\Phi \frac{dL(n)}{dn} = -(\Omega+4\Psi)\,L(n) + \Omega\,S(n) \qquad L(0)= \xi_{0,0}\,(\Omega+2\Psi)/\Phi \qquad (32)$$

$$2\Phi \frac{dS(n)}{dn} = -2\Omega\,S(n) + 4\Psi\,V(n) \qquad S(0)=0 \qquad (32)$$

$$2\Phi \frac{dV(n)}{dn} = -(2\Omega+4\Psi)\,V(n) + 2\Omega\,S(n) + 2\Omega\,L(n) \qquad V(0)=0 \qquad (33)$$

[0088] The instantaneous dead polymer chain length distribution is proportional to L_n, as evident from the species rate (R_{D_n}). Therefore through L_n the solution of the above system of differential equations gives the instantaneous dead polymer distribution X_n and the continuous distribution X(n) is similarly proportional to L(n).

$$\text{Instantaneous Dead Polymer Distribution, } X_n = R_{D_n} / \sum_{m=1}^{\infty} R_{D_m} = L_n / \sum_{m=1}^{\infty} L_m = L_n/\xi_{0,0} \qquad (34)$$

Solution for the Complete MWD Curve

[0089] The distribution functions of the increasing polymer chain length can be solved either numerically or analytically by persons familiar with the integration of ordinary differential equations. The analytical solution, although algebraically complicated, is given here because it agrees completely with the Moments Model (Equations (20) and (21)) while also predicting nuances in MWD such as peak location multi-modality, and tailing.

[0090] The software package known as *Mathematica*™ was used to develop an analytical solution to the system of ordinary differential equations that describe the propagating polymer distribution functions L(n), S(n), and V(n). The analytical solution for L(n) was used to describe the instantaneous dead polymer distribution X(n), by normalizing L(n) over its integral.

$$X(n) = L(n) / \int_0^{\infty} L(m)\,dm \qquad (35)$$

[0091] An explicit analytical solution for X(n) may be obtained using *Mathematica*™. The analytical solution for X(n) is described below as a function of parameters B_n and DP_{no}, and the solution may be restated in terms of R_c or B_n through the substitution $R_c = B_n = B_c/(1-B_c)$. (36)

[0092] The chain length distribution function X(n) is evaluated as follows from the definition of RootSum given by *Mathematica*™. The polynomial below has three roots which will be called x_1, x_2, and x_3. Two of the three roots of the polynomial are complex over the range of possible values of B_n.

$$0 = 1 + B_n + (3 + 5\,B_n + 2\,B_n^2)\,x + 3\,(1 + B_n)\,x^2 + x^3 \tag{37}$$

[0093] The roots x_1, x_2, and x_3 are used in the instantaneous dead chain length distribution function X(n).

$$X(n) = \left(\frac{1+B_n}{DP_{no}}\right) \sum_{i=1}^{3} \frac{(1 + 2\,x_i + B_n\,x_i + x_i^2)}{3 + 5\,B_n + 2\,B_n^2 + 6\,(1 + B_n)\,x_i + 3\,x_i^2}\, e^{x_i\, n/DP_{no}} \qquad (0 \le n \le \infty) \tag{38}$$

[0094] Various moments of X(n) are evaluated to give instantaneous number and weight average chain lengths (DP_n, DP_w) or molecular weights (M_n, M_w). The average chain lengths and weights resulting from the continuous distribution X(n) are equal to the moment model predictions given previously for long chain polymerization and a discrete distribution and are expressed below in terms of both B_c and B_n, where R_c=B_n.

$$DP_n = \frac{\int_0^\infty n\,X(n)\,dn}{\int_0^\infty X(n)\,dn} = \frac{DP_{no}}{1 - B_c} = DP_{no}\,(1+B_n) \qquad M_n = \frac{M_{no}}{1 - B_c} = M_{no}\,(1+B_n) \tag{39}$$

$$Z_p = \frac{DP_w}{DP_n} = \frac{M_w}{M_n} = \frac{\left(\int_0^\infty n^2\,X(n)\,dn\right)\left(\int_0^\infty X(n)\,dn\right)}{\left(\int_0^\infty n\,X(n)\,dn\right)^2} = 2 + 6\,B_c - 4\,B_c^2 = \frac{2 + 10\,B_n + 4\,B_n^2}{(1+B_n)^2} \tag{40}$$

[0095] Those skilled in the art of polymer reaction engineering are familiar with the use of predicted bulk polymer MWD models to create simulated Size Exclusion Chromatography (SEC) curves. Such a simulation is useful in relating how kinetics and recipes are expected to impact SEC measurements. The primary calibrated result of an SEC measurement is a table or plot of dw/dLog(M) versus Log(M), where M is species molecular weight or size and dw/dLog(M) is an indication of the relative amount of polymer corresponding to M. It is commonly accepted that this SEC result can be simulated by a table or plot of n^2 X(n) versus Log(M), where n^2 X(n) is expected to be proportional to dw/dLog(M).

[0096] FIG. 2 shows a series of simulated SEC curves wherein the level of diene "Ladder Branching" (B_c, B_n, R_c) is varied. The independent variable in FIG. 2 is scaled by linear molecular weight or chain length such that the plotting is universal and independent of starting molecular weight. The zero-branching case in FIG. 2 is the well-known "most probable" MWD (P.J. Flory, *J. Am. Chem. Soc.* **1936**, *58*, 1877) and is the expected MWD for linear addition co-polymerization performed under ideal homogeneous conditions.

[0097] A more detailed analysis of the peak MW values has been performed using a large series of branching levels applied to the MWD model. FIG. 3 shows a universal plot of relative peak MW as a function branching level. FIG. 3 demonstrates the low branching region of peak MW insensitivity ($0<R_c<0.15$) as well as the higher branching regime ($R_c \geq 0.15$) wherein the peak MW increases steadily with branching level.

Alternate Tri-Functional Dienes "Ladder Branching" Mechanism and Model

[0098] There are alternate mechanisms that can explain branching and MWD trends observed when dual chain catalysts incorporate dienes under desired conditions. While M_n is often observed to increase with dienes addition, some catalyst-diene combinations have been found to result in M_w increases while demonstrating little or no measurable M_n increase as diene levels are raised. One explanation for constant M_n is that a single beta-hydride elimination (or chain-transfer to hydrogen) might tend to occur immediately after the diene has inserted on both propagating chains. This scenario would result in the creation of tri-functional branches by the dienes insertion and, in pure form, would eliminate bridged propagating species (S_n) from the kinetics.

[0099] The kinetics scheme is modified to consider this alternative mechanism by substituting the following reactions for "Dienes Bridging".

	Reaction	Rate Constant
Tri-functional Diene Branching	$P_{n,m} + D \rightarrow P_{0,n+m} + br + kc$	$2\ k_d$, (L/mole/sec)
	$P_{n,m} + D \rightarrow P_{n+m,0} + br + kc$	$2\ k_d$, (L/mole/sec)

[00100] Any polymer reaction engineer skilled in the art of modeling and kinetics could re-derive the moments and MWD function model for these alternative kinetics using the same

sequence of assumptions as before. The resulting instantaneous dead chain length distribution function X(n) is given below for this tri-functional branching mechanism

$$X(n) = \left(\frac{\text{Cosh}[\frac{n\sqrt{B_c}}{DP_{no}(1-B_c)}] - \sqrt{B_c}\,\text{Sinh}[\frac{n\sqrt{B_c}}{DP_{no}(1-B_c)}]}{DP_{no}(1-B_c)} \right) e^{-n/(DP_{no}(1-B_c))} \qquad (0 \le n \le \infty) \qquad (41)$$

[00101] In Equation (41), B_c is defined as branch points per kinetic chain and DP_{no} is defined as the diene-free average linear chain length. The kinetic scheme assumes that the linear (kinetic) chain length actually decreases with dienes incorporation due to diene induced beta hydride elimination. Therefore, a good alternate indication of branching is B_n, which is defined as branch points per number average polymer molecule, where $B_c = B_n/(1+B_n)$. The function X(n) is easily rewritten in terms of B_n.

[00102] Integrations of X(n) gives results for instantaneous number and weight average chain lengths (DP_n, DP_w) or molecular weights (M_n, M_w). The average chain lengths and weights resulting from the continuous distribution X(n) are equal to a moment model predictions when long chain polymerization is assumed. Integration of X(n) confirms that DP_n and M_n are constant with respect to branching level (B_c or B_n). Integration of X(n) also shows how polydispersity is expected to vary with branching level when dienes are assumed to create tri-functional branches.

$$DP_n = \frac{\int_0^\infty n\,X(n)\,dn}{\int_0^\infty X(n)\,dn} = DP_{no} \qquad \text{therefore:} \qquad M_n = M_{no} \qquad (42)$$

$$Z_p = \frac{DP_w}{DP_n} = \frac{M_w}{M_n} = \frac{\left(\int_0^\infty n^2\,X(n)\,dn\right)\left(\int_0^\infty X(n)\,dn\right)}{\left(\int_0^\infty n\,X(n)\,dn\right)^2} = 2\,(1 + B_c) = \frac{2\,(1 + 2\,B_n)}{1 + B_n} \qquad (43)$$

[00103] The above relationship of polydispersity (M_w/M_n) to tri-functional branching level shows no instability or divergence at any branching level. Most surprising is that at high branching levels the polydispersity is predicted to level off at 4. Of course, this prediction is for an ideal co-polymerization and symmetric catalyst system with any non-idealities expected to give an increased polydispersity.

[00104] The chain length distribution function can again be used to construct predicted MWD curves. FIG. 4 is a series of simulated SEC curves wherein the level of tri-functional branching (B_c or B_n) is varied. The independent variable in FIG. 4 is scaled by linear molecular weight or chain length such that the plotting is universal and independent of starting molecular weight. The zero-branching case in FIG. 4 is the well-known "most probable" MWD and is expected for linear addition co-polymerization performed under ideal homogeneous conditions. FIG. 5 is a plot of relative peak MW for tri-functional dienes branching which demonstrates that the MWD peak is most sensitive to branching level at intermediate branching levels in the approximate range of $0.2<B_n<0.9$ or $0.17<B_c<0.5$.

Conventional Branching Models

[00105] The purpose of this section is to compare a variety of conventional dienes branching and random polymer coupling to the "Ladder Branching" models. The comparison demonstrates the inherent instability of conventional dienes branching and random polymer coupling in contrast to "Ladder Branching". The molecular architecture resulting from the dienes "Ladder Branching" is different from (a) the conventional Dienes Continuous Stirred Tank Reactor (CSTR) Branching Model, (b) conventional Dienes Semi-Batch Branching Model; (c) Polymer CSTR Coupling Model; and (d) Polymer Batch Coupling Model.

[00106] a) Conventional Dienes CSTR Branching Model Ver Strate-1980 (G. Ver Strate, C. Cozewith, W.W. Graessley, *J. App. Polym. Sci.* **1980**, *25*, 59), Guzman-2010 (J.D. Guzman, D.J. Arriola, T. Karjala, J. Gaubert, B.W.S. Kolthammer, *AIChE* **2010**, *56*, 1325):

$$Z_p = \frac{DP_w}{DP_n} = \frac{M_w}{M_n} = (1 - B_c)\left(\frac{1 - 4\,B_c - \sqrt{1 - 8\,B_c}}{(2\,B_c)^2}\right) = \frac{1 - 3\,B_n - \sqrt{(1 - 7\,B_n)(1 + B_n)}}{(2\,B_n)^2} \quad (44)$$

[00107] b) Conventional Dienes Semi-Batch Branching Model, Cozewith-1979 (C. Cozewith, W.W. Graessley, G. Ver Strate, *Chem. Eng. Sci.* **1979**, *34*, 245), and d) Polymer Batch Coupling Model, Cozewith-1979, Flory-1953 (P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953), Tobita-1995 (H. Tobita, *J. Polym. Sci. B* **1995**, *33*, 1191):

$$Z_p = \frac{DP_w}{DP_n} = \frac{M_w}{M_n} = \frac{2 - 2\,B_c}{1 - 4\,B_c} = \frac{2}{1 - 3\,B_n} \quad (45)$$

$$X(n) = e^{-n(1+2\,B_c)/DP_{no}} \left(\frac{1}{DP_{no}}\right) \sum_{b=0}^{\infty} \left(\frac{n}{DP_{no}}\right)^{3b} \frac{(2\,B_c)^b}{(1+b)!(1+2b)!} \quad (46)$$

[00108] c) Polymer CSTR Coupling Model:

$$Z_p = \frac{DP_w}{DP_n} = \frac{M_w}{M_n} = (1 - B_c)\left(\frac{1 - \sqrt{1 - 16\,B_c}}{4\,B_c}\right) = \frac{1 - \sqrt{(1 - 15\,B_n)/(1 + B_n)}}{4\,B_n} \quad (47)$$

Characterizing Tetra-functional Long-Chain Branched Polyolefin

[00109] Depending on the degree of branching, a variety of methods can either determine LCB, such as nuclear magnetic resonance (NMR), or distinguish the effect of LCB in the polymer. For example, the effect of LCB is observed in shear flow in the van Gurp-Palmen analysis, also an increase of the shear viscosity at low angular frequencies and strength of the shear thinning behavior can be attributed to LCB. In extensional flow, the influence of LCB is usually identified in the degree of hardening or the strength of the melt and the maximum deformation achieved. Other plots such as Mark-Houwink plots, broadening molecular weight distributions (MWD), and g'_{vis} plots provide additional information about LCB. A high level of natural LCB in a polymer is difficult to achieve due to the limited concentration of vinyl terminated polymers (maximum one per polymer chain) and the need to run to high conversion to ensure LCB formation. To ensure high conversion, there is a low ethylene concentration in the reactor, thus enabling a great amount of vinyl terminated polymers to be reinserted in a second polymer chain.

[00110] The conventional process of incorporating dienes into a polymer synthesis system suffers from the fundamental flaw of gel formation or reactor fouling at high branching levels. The kinetic modeling, discussed in previous paragraphs, may provide good predictive results that enable a better understanding of gel formation. For example, longer polymer chains have proportionally more pendant vinyls and polymer chains containing more pendant vinyls will more likely re-insert into the catalyst to form a LCB. Thus, the larger polymer chains preferentially re-insert forming tetra-functional branches, which are even larger polymer molecules, and a gel problem or instability results when the LCB level reaches a threshold value. A simulation of the weight average molecular weight (M_w) and number average molecular weight (M_n) as a function of conventional tetra-functional branching is shown in FIG. 1 for ethylene-based polymer in a semi-batch reactor at constant pressure. In FIG. 1, M_n only

marginally increases as M_w becomes infinite. In this example, as the M_w increases to a number greater than 200,000 grams per mole (g/mol), the polymer molecular weight distribution (MWD) becomes unstable and gels begin to form. The MWD is defined by the weight average molecular weight, M_w, divided by the number average molecular weight, M_n, (M_w/M_n).

[00111] Polymer gels are narrowly defined for the purpose of this disclosure to be a polymer fraction that is phase separated due to its high branching level and/or high molecular weight. Polymer gels can be observed in solution or in the melt and tend to interfere with properties such as optical clarity and film and fiber performance. Polyethylene interpolymer gels can be measured by degree of polymer insolubility in hot xylene. Gels content is often correlated to and therefore estimated from GPC polymer recovery percentage. When polymer gels form, they may deposit within the reactor and result in fouling.

[00112] FIG. 7 and FIG. 8 show the differences in the MWD curves expected from conventionally branched and "Ladder Branched" polymers. A series of metrics describing MWD characteristics has been developed from a study of MWD data and comparison to MWD models. Each of the MWD descriptive metrics presented here is independent of average MW and is focused on the high MW portion of the MWD. The MWD metrics are derived from a scaled MWD curve (dW/dlogM) with the primary or highest peak of the MWD defined as having a value of unity. If more than one peak have the same height, the highest MW peak is the primary peak. The independent variable in the MWD curve is Log(M), which is the logarithm of M to base 10. The metrics will be defined and presented as a function of M_w/M_{wo} and M_p/M_{po} which can be translated to branches per molecule or segment using FIG. 6, FIG. 7, FIG. 8, and FIG. 9. One skilled in the art of GPC data interpretation would understand these metrics and would be able to calculate them from GPC data.

[00113] A family of GPC shape metrics, G(A/B), are calculated from the slopes at defined points on the right hand side of the MWD curve, where S(A) and S(B) are the first occurrences of these slopes to the right of the primary peak at A% and B% of the height of the primary peak. The points A and B are selected as pairs that would have nearly the same slope if the MWD were "most probable". A depiction of these points and their slope is shown in the graph of FIG. 10 for a most probable MWD. These slope pairs S(A) and S(B) are used together to calculate a function G(A/B) resembling a second derivative, which will be shown to be a useful metric to differentiate "Ladder Branched" MWDs from conventionally or randomly branched MWDs.

Values of G(79/29) and G(96/08) describe the change in slope of the right hand side (RHS) of the MWD and are defined below from the high MW slopes:

$$G(79/29) = (S(79) - S(29)) / S(79) \quad (48)$$

$$G(96/08) = (S(96) - S(8)) / S(96) \quad (49)$$

[00114] The shape metrics G(79/29) and G(96/08) are tested on the MWD models for tetra-functional "Ladder Branching" and conventional dienes branching with the results plotted in FIG. 11, FIG. 12, FIG. 13, FIG. 14. The figures indicate that conventional branching gives G(79/29) and G(96/08) values that increase steadily as MW responds to branching. However, when applied to "Ladder Branching", these shape metrics fall precipitously at low levels of branching (low M_w/M_{wo}) then approach zero at moderate to high levels of branching. That is not surprising, since the high MW portion of a "Ladder Branched" MWD resembles a most probable MWD.

[00115] FIG. 11, FIG. 12, FIG. 13, and FIG. 14 depict a similar response of G(79/29) and G(96/08) metrics to branching, however, the G(96/08) metric is expected to be more sensitive to high MW tailing that would result from conventional dienes branching. The term "high MW tailing" or "high molecular weight tail" refers to the high molecular weight fraction as shown by the conventional GPC and the absolute GPC. Depending on catalyst-diene pairing and experimental conditions, one might expect a "Ladder Branched" system to have some conventional branching thereby raising the shape metric value above that expected for pure "Ladder Branching".

[00116] MWD Area Metrics

[00117] Visual inspections of the "Ladder Branched" MWD show that there is a characteristic lack of a high MW tail normally seen for branched polymers. FIG. 16 and FIG. 17 demonstrate how the model predicts a lack of tailing for "Ladder Branched" polymers. The "Ladder Branching" MWD data shows the characteristic lack of tail for many experiments but also indicates some tail formation is possible depending on polymerization conditions and diene/catalyst pairing.

[00118] Polydispersity indices (M_w/M_n, M_z/M_w, etc) are known metrics for tailing, but are not preferred due to their sensitivity to low MWD artifacts. Therefore, a more focused version of the

polydispersity indices is used to develop a standard for which the integrals are performed only on the high MW portion of the MWD. The M_w/M_n and M_z/M_w metrics are successful in differentiating dienes "Ladder Branching" from conventional branching and are very sensitive to high MW baseline selection and baseline noise.

[00119] The area under the MWD curve is relatively insensitive to baseline issues as compared to the higher moments required to calculate MWD dispersity indices (M_w/M_n, M_z/M_w, etc). Therefore, it was decided that metrics be developed which entail the non-weighted integration of the MWD. These MWD area metrics, A_{HIGH} and A_{TAIL}, are calculated from the GPC curve areas for defined regions on the right hand side of the MWD curve. The MWD area metrics (A_{HIGH} and A_{TAIL}) are derived from a scaled MWD curve (dW/logM) with the primary or highest peak of the MWD defined as having a value of unity. If more than one peak have the same height, the highest MW peak is the primary peak. The independent variable in the MWD curve is Log(M), which is the logarithm of M to base 10. Both of the MWD area metrics depend on the point of maximum slope of the high MW portion of the MWD. The quantities and limits necessary for evaluating the area metrics are listed below, and demonstrated in FIG. 15 for a most probable MWD.

[00120] S_{max} = first instance of a maximum downward slope on the RHS (higher MW side) of the primary peak (absolute value of the slope) of the scaled MWD

[00121] H_{smax} = height of the scaled MWD at the point of maximum slope

[00122] pt1 = LogM value of S_{max}

[00123] pt2 = LogM value where the S_{max} tangent crosses the x-axis

[00124] The MWD area metrics are defined below, where A_{HIGH} is merely the area of the MWD region falling after the point of maximum slope. The second area metric, A_{TAIL}, is the small high MW area depicted in FIG. 15, and is evaluated by subtracting a triangular area from A_{HIGH}.

$$A_{HIGH} = \int_{pt1}^{\infty} MWD \, dLogM \tag{50}$$

$$A_{TAIL} = A_{HIGH} - \tfrac{1}{2} (H_{smax})^2/S_{max} \tag{51}$$

[00125] The area metrics A_{HIGH} and A_{TAIL} have been tested on the MWD models for "Ladder Branching" and conventional dienes branching with the results plotted in FIG. 16, FIG. 17, FIG. 18, and FIG. 19. The plots show that the high MW area, as defined by A_{HIGH} or A_{TAIL}, increases dramatically as the conventional branching level is increased. However, the "Ladder Branching" model predicts that the high MW area metrics (A_{HIGH} or A_{TAIL}) are almost unaffected by "Ladder Branching" level. The values of A_{HIGH} and A_{TAIL} for a most probable MWD are about 0.07 and 0.015, respectively. Example MWD data will demonstrate that the dienes-free linear polymers tend to have slightly higher values of A_{HIGH} and A_{TAIL} due to non-ideal aspects of the polymerization. Example data also show a variety of highly branched "Ladder Branched" polymers with essentially no high MW tail beyond what is expected from a most probable MWD. The high MW area metrics also are diagnostic of slight levels of high MW tail formation that "Ladder Branched" polymer can exhibit when accompanied by a degree of conventional branching. The metric A_{TAIL} is less influenced by linear MWD non-ideality than A_{HIGH}. However, in theory A_{HIGH} and A_{TAIL} metrics are equally indicative of high MW tail formation.

Tetra-functional Long-Chain Branched Polyolefin

[00126] Polymers produced from the "Ladder Branching", as described in Scheme 4, are included in this disclosure.

[00127] In embodiments, the ethylene-based polymers of this disclosure include a melt viscosity ratio or rheology ratio ($V_{0.1}/V_{100}$) at 190 °C of at least 10, where $V_{0.1}$ is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 100 radians/second. In one or more embodiments, the melt viscosity ratio is at least 14, at least 20, at least 25, or at least 30. In some embodiments, the melt viscosity ratio is greater than 50, at least 60, or greater than 100. In some embodiments, the melt viscosity ratio is of from 14 to 200.

[00128] The "rheology ratio" and "melt viscosity ratio" are defined by $V_{0.1}/V_{100}$ at 190 °C, where $V_{0.1}$ is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 0.1 radians/second, and V_{100} is the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 100 radians/second.

[00129] In one or more embodiments, the ethylene-based polymers of this disclosure have an Average g' less than 0.86, where the Average g' is an intrinsic viscosity ratio determined by gel

permeation chromatography using a triple detector. In some embodiments, the ethylene-based polymers of this disclosure have an Average g' from 0.64 to 0.86. All individual values and subranges encompassed by "from 0.64 to 0.86" are disclosed herein as separate embodiments; for example, the Average g' of the ethylene-based polymer may range from 0.64 to 0.75, from 0.68 to 0.79, or from 0.65 to 0.83. In one or more embodiments, the Average g' is from 0.65 to 0.84, from 0.66 to 0.82, or from 0.66 to 0.80.

[00130] In some embodiments, the ethylene-based polymers have a G(79/29) value of less than or equal to 0.035 as determined from a gel permeation chromatography curve having a peak height, a slope M79 at 79% of the peak height, and a slope M29 at 29% of the peak height, wherein the G(79/29) value equals (M79– M29) / M79. All individual values and subranges encompassed by "of less than or equal to 0.035" are disclosed herein as separate embodiments; for example, "of less than or equal to 0.035" includes from greater than 0.0 to 0.035, from 0.010 to 0.034, and includes negative values. In one or more embodiments, the ethylene-based polymer of this disclosure may have a G(79/29) value of less than or equal to 0.030 as determined from a gel permeation chromatography curve.

[00131] In one or more embodiments, the melt viscosity ratio of the ethylene-based polymer of this disclosure may be greater than ten times the elasticity factor where the melt viscosity ratio ($V_{0.1}/V_{100}$) is determined by $V_{0.1}$, the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 0.1 radians/second, and V_{100}, the viscosity of the ethylene-based polymer at 190 °C at an angular frequency of 100 radians/second, and the elasticity factor m is [((tan ($\delta_{0.1}$) - tan (δ_{100}))*1000)/(0.1-100))], wherein tan ($\delta_{0.1}$) is the tangent of the phase angle at 0.1 radians/second, and tan (δ_{100}) is the tangent of the phase angle at 100 radians/second.

[00132] In one or more embodiments, the ethylene-based polymer may have an elasticity factor m at 190°C that is less than or equal to 8 seconds/radian, where m is [((tan ($\delta_{0.1}$) - tan (δ_{100}))*1000)/(0.1-100))]. In other embodiments, the ethylene-based polymer may have an elasticity factor m at 190°C that is less than or equal to 4 seconds/radian.

[00133] In various embodiments, the melt strength of the ethylene-based polymer of this disclosure may be greater than 6 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). In some embodiments, the melt strength of the ethylene-based polymer may be greater than 10 cN.

[00134] In embodiments, the ethylene-based polymer may have a molecular weight tail quantified by an MWD area metric A_{TAIL}, and A_{TAIL} is less than or equal to 0.04. All individual values and subranges encompassed by "less than or equal to 0.04" are disclosed herein as separate embodiments. For example, in some embodiments, the A_{TAIL} of the ethylene-based polymer of this disclosure is greater than 0 and less than or equal to 0.03 as determined by gel permeation chromatography using a triple detector.

[00135] In embodiments, the M_w of ethylene-based polymer may be less than or equal to 800,000 Daltons, as determined by gel permeation chromatography using a triple detector. In one or more embodiments, the M_w of the ethylene-based polymer may be less than or equal to 400,000 Daltons.

[00136] In various embodiments, the ethylene-based polymer may have an M_p/M_{p0} greater than 1.20, where M_p is the peak molecular weight of the ethylene-based polymer as determined from conventional gel permeation chromatography, and M_{p0} is the initial peak molecular weight of the ethylene-based polymer without polyene comonomer.

[00137] In embodiments, the ethylene-based polymer has a M_w/M_{w0} of greater than 1.20, in which M_w is the weight average molecular weight of the ethylene-based polymer as determined from a GPC curve of the ethylene-based polymer acquired by gel permeation chromatography. M_{w0} is the initial weight average molecular weight of a comparative ethylene-based polymer by gel permeation chromatography. The comparative ethylene-based polymer is a reaction product of polymerizing ethylene monomer and all C_3 to C_{14} comonomers present in the ethylene-based polymer, if any, without the at least one polyene comonomer, under the defined polymerization reaction conditions.

[00138] Each M_{w0} and the M_{p0} is a metric of polymer resins without the addition of diene into the reactor during polymerization, as previously discussed. Each subsequent addition of diene produces a polymer resin from which the metric M_w or M_p may be determined. The amount of diene incorporated into the reactor is small in comparison to the other reactants in the reactor. Therefore, the addition of diene does not affect the total amount of comonomer, ethylene, and solvent in the reactor.

[00139] In various embodiments, the ethylene-based polymer has a gpcBR branching index of from 0.1 to 3.0. All individual values and subranges encompassed by "from 0.10 to 3.00" are disclosed herein as separate embodiments; for example, the ethylene-based polymers, may include a gpcBR branching index of from 0.10 to 2.00, from 0.10 to 1.00, from 0.15 to 0.65, from 0.20 to 0.75, or 0.10 to 0.95.

[00140] The long-chain branching polymerization processes described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene and propylene. In some embodiments, there is only a single type of olefin or α-olefin in the polymerization scheme, creating what is essentially a homopolymer with small amounts of incorporated diene comonomer. However, additional α-olefins may be incorporated into the polymerization procedure. The additional α-olefin co-monomers typically have no more than 20 carbon atoms. For example, the α-olefin co-monomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary α-olefin co-monomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-1-pentene, and ethylidene norbornene. For example, the one or more α-olefin co-monomers may be selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-hexene and 1-octene.

[00141] The long-chain branched polymer, for example homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α-olefins, may comprise at least 50 percent by weight of units derived from ethylene. All individual values and subranges encompassed by "from at least 50 weight percent" are disclosed herein as separate embodiments; for example, the ethylene-based polymers, homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α-olefins may comprise at least 60 percent by weight of units derived from ethylene; at least 70 percent by weight of units derived from ethylene; at least 80 percent by weight of units derived from ethylene; or from 50 to 100 percent by weight of units derived from ethylene; or from 80 to 100 percent by weight of units derived from ethylene.

[00142] In some embodiments of the ethylene-based polymers, the ethylene-based polymer includes additional α-olefin. The amount of additional α-olefin in the ethylene-based polymer is less than or equal to 50 mole percent (mol%); other embodiments the amount of additional α-olefin includes at least 0.01 mol% to 25 mol%; and in further embodiments the amount of

additional α-olefin includes at least 0.1 mol% to 10 mol%. In some embodiments, the additional α-olefin is 1-octene.

[00143] In some embodiments, the long-chain branched polymers may comprise at least 50 percent by moles of units derived from ethylene. All individual values and subranges from at least 90 mole percent are included herein and disclosed herein as separate embodiments. For example, the ethylene based polymers may comprise at least 93 percent by moles of units derived from ethylene; at least 96 percent by moles of units; at least 97 percent by moles of units derived from ethylene; or in the alternative, from 90 to 100 percent by moles of units derived from ethylene; from 90 to 99.5 percent by moles of units derived from ethylene; or from 97 to 99.5 percent by moles of units derived from ethylene.

[00144] In some embodiments of the long-chain branched polymer, the amount of additional α-olefin is less than 50%; other embodiments include at least 1 mole percent (mol%) to 20 mol%; and in further embodiments the amount of additional α-olefin includes at least 5 mol% to 10 mol%. In some embodiments, the additional α-olefin is 1-octene.

[00145] Any conventional polymerization processes may be employed to produce the long-chain branched polymer. Such conventional polymerization processes include, but are not limited to, solution polymerization processes, gas phase polymerization processes, slurry phase polymerization processes, and combinations thereof using one or more conventional reactors such as loop reactors, isothermal reactors, fluidized bed gas phase reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[00146] In one embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a single loop reactor system, wherein ethylene and optionally one or more α-olefins are polymerized in the presence of the catalyst system, as described herein, and optionally one or more co-catalysts. In another embodiment, the ethylene-based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α-olefins are polymerized in the presence of the catalyst system in this disclosure, and as described herein, and optionally one or more other catalysts. The catalyst system, as described herein, can be used in the first reactor, or second reactor, optionally in combination with one or more other catalysts. In one embodiment, the ethylene-based polymer may be produced via solution polymerization in

a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α-olefins are polymerized in the presence of the catalyst system, as described herein, in both reactors.

[00147] In another embodiment, the long-chain branched polymer may be produced via solution polymerization in a single reactor system, for example a single loop reactor system, in which ethylene and optionally one or more α-olefins are polymerized in the presence of the catalyst system, as described within this disclosure, and optionally one or more co-catalysts, as described in the preceding paragraphs. In some embodiments, the long-chain branching polymerization process for producing the long-chain branched polymer includes polymerizing ethylene and at least one additional α-olefin in the presence of a catalyst system.

[00148] The long-chain branched polymers may further comprise one or more additives. Such additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, pigments, primary antioxidants, secondary antioxidants, processing aids, UV stabilizers, and combinations thereof. The ethylene-based polymers may contain any amounts of additives. The ethylene-based polymers may compromise from about 0 to about 10 percent by the combined weight of such additives, based on the weight of the ethylene based polymers and the one or more additives. The ethylene-based polymers may further comprise fillers, which may include, but are not limited to, organic or inorganic fillers. The long-chain branched polymers may contain from about 0 to about 20 weight percent fillers such as, for example, calcium carbonate, talc, or $Mg(OH)_2$, based on the combined weight of the ethylene based polymers and all additives or fillers. The ethylene-based polymers may further be blended with one or more polymers to form a blend.

[00149] In some embodiments, the long-chain polymerization process for producing long-chain branched polymers may include polymerizing ethylene and at least one additional α-olefin in the presence of a catalyst having two polymer producing sites. The long-chain branched polymer resulting from such the catalyst having two polymer producing sites may have a density according to ASTM D792 (incorporated herein by reference in its entirety) from 0.850 g/cm^3 to 0.960 g/cm^3, from 0.880 g/cm^3 to 0.920 g/cm^3, from 0.880 g/cm^3 to 0.910 g/cm^3, or from 0.880 g/cm^3 to 0.900 g/cm^3, for example.

[00150] In another embodiment, the long-chain branched polymer resulting from the long-chain polymerization process may have a melt flow ratio (I_{10}/I_2) from 5 to 100, in which melt index I_2 is measured according to ASTM D1238 (incorporated herein by reference in its entirety) at 190 °C and 2.16 kg load, and melt index I_{10} is measured according to ASTM D1238 at 190 °C and 10 kg load. In other embodiments the melt flow ratio (I_{10}/I_2) is from 5 to 50, in others, the melt flow ratio is from 5 to 25, in others, the melt flow ratio is from 5 to 9.

[00151] In some embodiments, the long-chain branched polymer resulting from the long-chain polymerization process may have a molecular-weight distribution (MWD) from 1 to 20, where MWD is defined as M_w/M_n with M_w being a weight average molecular weight and M_n being a number average molecular weight. In other embodiments, the polymers resulting from the catalyst system have a MWD from 1 to 10. Another embodiment includes a MWD from 1 to 3; and other embodiments include MWD from 1.5 to 2.5.

Parallel Polymerization Reactor (PPR)

[00152] The small scale solution polymerization examples are performed in 15 mL vials using a total liquid volume of 5 mL, a constant ethylene pressure of 150 psig, and a polymerization temperature of 120 °C. The 5 mL liquid volume consists of a 0.84 mL comonomer mixture containing 500 nmol MMAO-3A, catalyst and activator solution in toluene, with sufficient Isopar-E added to achieve a 5 mL liquid volume. Hydrogen (H_2) was added to the reaction mixture by simultaneously pre-pressurizing the empty reaction vials with 20±3 psig H_2 at 80 °C, such that experiments for any given diene are performed with the same H_2 load. All liquid volumes were dispensed at room temperature and added volumetrically in relation to the 5 mL total volume. The catalyst was added last to the reaction mixture as a 5 mM solution in toluene which was separately activated by 1.5 equivalents of Co-Catalyst A (methyldi(tetradecyl)ammonium tetrakis(pentafluorophenyl)borate). The comonomer solution was composed predominantly of 1-octene with a minor (0-6%) volume fraction of a diene species. The polymerizations were run for times not exceeding about 30 minutes and were quenched by CO addition followed by vial de-pressurization.

Gel Permeation Chromatography (GPC) (Conventional GPC)

[00153] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5)

and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 160° Celsius and the column compartment was set at 150° Celsius. The columns used were 4 Agilent "Mixed A" 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[00154] Calibration of the GPC column set was performed with at least 20 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 and were arranged in 6 "cocktail" mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were dissolved at 80 degrees Celsius with gentle agitation for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 52 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

$$M_{polyethylene} = A \times \left(M_{polystyrene}\right)^{B} \quad (52)$$

where M is the molecular weight, A has a value of 0.4315 and B is equal to 1.0.

[00155] A polynomial between 3rd and 5th order was used to fit the respective polyethylene-equivalent calibration points. A small adjustment to A (from approximately 0.415 to 0.44) was made to correct for column resolution and band-broadening effects such that NIST standard NBS 1475 is obtained at 52,000 Mw.

[00156] The total plate count of the GPC column set was performed with Eicosane (prepared at 0.04 g in 50 milliliters of TCB and dissolved for 20 minutes with gentle agitation). The plate count (Equation 53) and symmetry (Equation 54) were measured on a 200 microliter injection according to the following equations:

$$Plate\ Count = 5.54 * \left(\frac{(\mathrm{RV}_{\mathrm{Peak\ Max}}}{Peak\ Width\ at\ \frac{1}{2} height}\right)^2 \quad (53)$$

where RV is the retention volume in milliliters, the peak width is in milliliters, the peak max is the maximum height of the peak, and ½ height is ½ height of the peak maximum.

$$Symmetry = \frac{(Rear\ Peak\ RV_{one\ tenth\ height} - RV_{Peak\ max})}{(RV_{Peak\ max} - Front\ Peak\ RV_{one\ tenth\ height})} \quad (54)$$

where RV is the retention volume in milliliters and the peak width is in milliliters, Peak max is the maximum position of the peak, one tenth height is 1/10 height of the peak maximum, and where rear peak refers to the peak tail at later retention volumes than the peak max and where front peak refers to the peak front at earlier retention volumes than the peak max. The plate count for the chromatographic system should be greater than 24,000 and symmetry should be between 0.98 and 1.22.

[00157] Samples were prepared in a semi-automatic manner with the PolymerChar "Instrument Control" Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200 ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160° Celsius under "low speed" shaking.

[00158] The calculations of $M_{n(GPC)}$, $M_{w(GPC)}$, and $M_{z(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 55-57, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i).

$$Mn_{(GPC)} = \frac{\sum_{i}^{i} IR_i}{\sum_{i}^{i} \left(IR_i / M_{polyethylene_i} \right)} \quad (55)$$

$$Mw_{(GPC)} = \frac{\sum_{i}^{i}\left(IR_i * M_{polyethylene_i}\right)}{\sum_{i}^{i} IR_i} \quad (56)$$

$$Mz_{(GPC)} = \frac{\sum_{i}^{i}\left(IR_i * M_{polyethylene_i}^{2}\right)}{\sum_{i}^{i}\left(IR_i * M_{polyethylene_i}\right)} \quad (57)$$

[00159] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. To facilitate the highest accuracy of a RV measurement of the flow marker peak, a least-squares fitting routine is used to fit the peak of the flow marker concentration chromatogram to a quadratic equation. The first derivative of the quadratic equation is then used to solve for the true peak position. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 58. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-2% of the nominal flowrate.

$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)}) \quad (58)$$

Triple Detector GPC (TDGPC) (Absolute GPC)

[00160] The chromatographic system, run conditions, column set, column calibration and calculation conventional molecular weight moments and the distribution were performed according to the method described in Gel Permeation Chromatography (GPC).

[00161] For the determination of the viscometer and light scattering detector offsets from the IR5 detector, the Systematic Approach for the determination of multi-detector offsets is done in

a manner consistent with that published by Balke, Mourey, et. al. (Mourey and Balke, Chromatography Polym. Chpt 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, Chromatography Polym. Chpt 13, (1992)), optimizing triple detector log (MW and IV) results from a broad homopolymer polyethylene standard ($M_w/M_n > 3$) to the narrow standard column calibration results from the narrow standards calibration curve using PolymerChar GPCOne™ Software.

[00162] The absolute molecular weight data is obtained in a manner consistent with that published by Zimm (Zimm, B.H., J. Chem. Phys., 16, 1099 (1948)) and Kratochvil (Kratochvil, P., Classical Light Scattering from Polymer Solutions, Elsevier, Oxford, NY (1987)) using PolymerChar GPCOne™ software. The overall injected concentration, used in the determination of the molecular weight, is obtained from the mass detector area and the mass detector constant, derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards of known weight average molecular weight. The calculated molecular weights (using GPCOne™) are obtained using a light 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 (IR5) and the light scattering constant (determined using GPCOne™) may be determined from a linear standard with a molecular weight in excess of about 50,000 g/mole. The viscometer calibration (determined using GPCOne™) may be accomplished using the methods described by the manufacturer, or, alternatively, by using the published values of suitable linear standards, such as Standard Reference Materials (SRM) 1475a (available from National Institute of Standards and Technology (NIST)). A viscometer constant (obtained using GPCOne™) is calculated which relates specific viscosity area (DV) and injected mass for the calibration standard to its intrinsic viscosity. The chromatographic concentrations are assumed low enough to eliminate addressing 2nd viral coefficient effects (concentration effects on molecular weight).

[00163] The absolute weight average molecular weight ($M_{w(Abs)}$) is obtained (using GPCOne™) from the Area of the Light Scattering (LS) integrated chromatogram (factored by the light scattering constant) divided by the mass recovered from the mass constant and the mass detector (IR5) area. The molecular weight and intrinsic viscosity responses are linearly extrapolated at chromatographic ends where signal to noise becomes low (using GPCOne™). Other respective moments, $M_{n(Abs)}$ and $M_{z(Abs)}$ are be calculated according to equations 59-60 as follows :

$$Mn_{(Abs)} = \frac{\sum_{i}^{i} IR_i}{\sum_{i}^{i} \left(IR_i / M_{Absolute\,i} \right)} \tag{59}$$

$$Mz_{(Abs)} = \frac{\sum_{i}^{i} \left(IR_i * M_{Absolute\,i}{}^{2} \right)}{\sum_{i}^{i} \left(IR_i * M_{Absolute\,i} \right)} \tag{60}$$

g'$_{ave}$ Values

[00164] g' is defined as the viscosity of a branched polymer divided by the viscosity of a linear polymer at the same MW:

$$g' = \frac{[\eta]_{branched}}{[\eta]_{linear}} |_{same\ M} \tag{61}$$

[00165] g'$_{ave}$ or average g' is the weight-averaged value of g' (B.H. Zimm, W.H. Stockmayer, *J. Chem. Phys.* **1949**, *17*, 1301).

Dynamic Mechanical Spectrum (or Small Angle Oscillatory Shear)

[00166] The complex viscosity (η*), moduli (G', G"), tan delta, and phase angle (δ) are obtained by dynamic oscillatory frequency sweep test in a frequency range from 0.1 to 100 rad/s, at 190 °C. The level of strain is set within the linear viscoelastic regime as identify by a strain sweep test at 100 rad/s at 190 °C. Tests are performed with stainless steel parallel plates of 25 mm diameter on a strain controlled rheometer ARES-G2 by TA Instruments. Samples of 3.3 mm thickness are squeezed and then trimmed in two steps prior to the actual test. In the first step, the sample are allowed to melt for 2.5 min, squeezed to 3 mm gap and trimmed. After an additional 2.5 min of soak time at 190 °C, the sample are squeezed to 2 mm gap, and the excess of material trimmed. The method has an additional five minute delay built in to allow the system to reach thermal equilibrium. Tests are performed under nitrogen atmosphere.

gpcBR Branching Index by Triple Detector GPC (TDGPC)

[00167] The gpcBR branching index was determined by first calibrating the light scattering, viscosity, and concentration detectors as described previously. Baselines were then subtracted from the light scattering, viscometer, and concentration chromatograms. Integration windows were 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 were then used to establish polyethylene and polystyrene Mark-Houwink constants. Upon obtaining the constants, the two values were 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 (62) and (63):

$$M_{PE} = \left(\frac{K_{PS}}{K_{PE}}\right)^{1/(\alpha_{PE}+1)} \cdot M_{PS}^{(\alpha_{PS}+1)/(\alpha_{PE}+1)} \tag{62}$$

$$[\eta]_{PE} = K_{PS} \cdot M_{PS}^{\alpha+1} \Big/ M_{PE} \tag{63}$$

[00168] 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 Poly-olefin Characterization," *Macromol. Symp.*, **2007**, *257*, 29-45. The index avoids the "slice-by-slice" TDGPC calculations traditionally used in the determination of g' values and branching frequency calculations, in favor of whole polymer detector areas. From TDGPC 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 TDGPC, sample intrinsic viscosities were also obtained independently using Equation (64). The area calculation in this case offers more precision, because, as an overall sample area, it is much less sensitive to variation caused by detector noise and TDGPC settings on baseline and integration limits. More importantly, the peak area calculation was not affected by the detector volume offsets. Similarly, the high-precision, sample intrinsic viscosity (IV) was obtained by the area method in Equation (64):

$$IV = [\eta] = \sum_i w_i IV_i = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \frac{\sum_i C_i IV_i}{\sum_i C_i} = \frac{\sum_i DP_i}{\sum_i C_i} = \frac{DP\ Area}{Conc.\ Area} \quad (64),$$

[00169] In Equation (64), DPi 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 was used to determine the molecular weight of the sample. The viscosity detector elution area for the sample polymer was used to determine the intrinsic viscosity (IV or [η]) of the sample. Initially, the molecular weight and intrinsic viscosity for a linear polyethylene standard sample, such as SRM1475a or an equivalent, were determined using the conventional calibrations ("cc") for both molecular weight and intrinsic viscosity as a function of elution volume:

$$[\eta]_{CC} = \sum_i \left(\frac{C_i}{\sum_i C_i} \right) IV_i = \sum_i w_i IV_{cc,i} \quad (65).$$

Equation (66) was used to determine the gpcBR branching index:

$$gpcBR = \left[\left(\frac{[\eta]_{CC}}{[\eta]} \right) \cdot \left(\frac{M_W}{M_{W,CC}} \right)^{\alpha_{PE}} - 1 \right] \quad (66),$$

wherein [η] is the measured intrinsic viscosity, $[\eta]_{cc}$ is the intrinsic viscosity from the conventional calibration (or conv GPC), Mw is the measured weight average molecular weight, and $M_{w,cc}$ is the weight average molecular weight of the conventional calibration. The weight average molecular weight by light scattering (LS) is commonly referred to as "absolute weight average molecular weight" or "M_w(abs)." The $M_{w,cc}$ from 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(conv)."

[00170] All statistical values with the "cc or conv" subscript are determined using their respective elution volumes, the corresponding conventional calibration as previously described, and the concentration (Ci). 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.

[00171] Previously, the procedure was repeated using the branched samples. The branched samples were analyzed using the final Mark-Houwink constants as the best "cc" calibration values.

[00172] The interpretation of gpcBR is straight forward. For linear polymers, gpcBR 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 TDGPC 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.

Batch Reactor Polymerization Procedure

[00173] The batch reactor polymerization reactions are conducted in a 2 L Parr™ batch reactor. The reactor is heated by an electrical heating mantle, and is cooled by an internal serpentine cooling coil containing cooling water. Both the reactor and the heating/cooling system are controlled and monitored by a Camile™ TG process computer. The bottom of the reactor is fitted with a dump valve that empties the reactor contents into a stainless steel dump pot. The dump pot is prefilled with a catalyst kill solution (typically 5 mL of an Irgafos / Irganox / toluene mixture). The dump pot is vented to a 30 gallon blow-down tank, with both the pot and the tank purged with nitrogen. All solvents used for polymerization or catalyst makeup are run through solvent purification columns to remove any impurities that may affect polymerization. The 1-octene and IsoparE are passed through two columns, the first containing A2 alumina, the second containing Q5. The ethylene is passed through two columns, the first containing A204

alumina and 4Å molecular sieves, the second containing Q5 reactant. The N_2, used for transfers, is passed through a single column containing A204 alumina, 4Å molecular sieves and Q5.

[00174] The reactor is loaded first from the shot tank that may contain IsoparE solvent and/or 1-octene, depending on reactor load. The shot tank is filled to the load set points by use of a lab scale to which the shot tank is mounted. After liquid feed addition, the reactor is heated up to the polymerization temperature set point. If ethylene is used, it is added to the reactor when the ethylene is at the reaction temperature to maintain reaction pressure set point. The amount of ethylene added is monitored by a micro-motion flow meter (Micro Motion). For some experiments, the standard conditions at 150 °C are 13 g ethylene, 15 g 1-octene, 240 psi hydrogen in 585 g of IsoparE, and the standard conditions at 150 °C are 15 g ethylene, 45 g 1-octene, 200 psi hydrogen in 555 g of IsoparE.

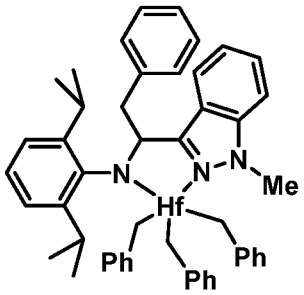
[00175] The procatalyst and activators are mixed with the appropriate amount of purified toluene to achieve a desired molarity solution. The procatalyst and activators are handled in an inert glove box, drawn into a syringe and pressure transferred into the catalyst shot tank. The syringe is rinsed three times with 5 mL of toluene. Immediately after the catalyst is added, the run timer begins. If ethylene is used, it is added by the Camile to maintain reaction pressure set point in the reactor. The polymerization reactions are run for 10 minutes, then the agitator is stopped, and the bottom dump valve is opened to empty reactor contents to the dump pot. The contents of the dump pot are poured into trays and placed in a lab hood where the solvent was evaporated off overnight. The trays containing the remaining polymer are transferred to a vacuum oven, where they are heated up to 140 °C under vacuum to remove any remaining solvent. After the trays cool to ambient temperature, the polymers were weighed for yield to measure efficiencies, and submitted for polymer testing.

EXAMPLES

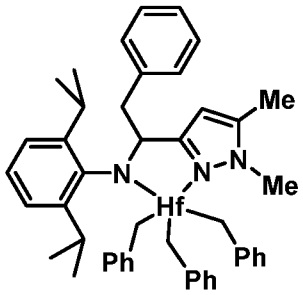
Tetra-functional Branching in the presence of various multi-chain catalysts and various dienes

[00176] The results of the small scale polymerizations are summarized in Table 3 through Table 7 (experimental is in the parallel polymerization reactors, PPR). The polymer results recorded in Table 3 through Table 7 were produced by polymerizing ethylene, octene, and a diene species in the presence of multi-chain catalysts and single chain catalyst controls. The polymer results in each table of the Table 3 through Table 7 were the product of various

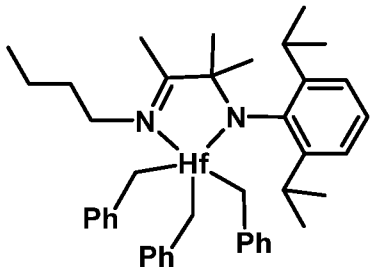
catalysts and diene species. The results in Table 3 are based on the polymer products of 3-methyl-1,4-pentadiene, ethylene, and octene in the presence of Comparative Catalyst C1 ("Comp. Cat. C1"), Catalyst 1 ("Cat. 1"), and Catalyst 2 ("Cat. 2"). The results in Table 4 are based on the polymer products of 1,4-pentadiene, ethylene, and octene in the presence of Cat. 2 and Catalyst 4 ("Cat. 4"). The results in Table 5 are based on the polymer products of 1,5-hexadiene, ethylene, and octene in the presence of Comp. Cat. C1, Catalyst 3 ("Cat. 3"), Catalyst 5 ("Cat. 5"), and Catalyst 6 ("Cat. 6"). The results in Table 6 are based on the polymer products of 1,7-octadiene, ethylene, and octene in the presence of Comp. Cat. C1, Cat. 6, Cat. 2, and Cat. 4. The results in Table 7 are based on the polymer products of 1,9-decadiene, ethylene, and octene in the presence of Cat. 3, Cat. 5, Cat. 6, and Cat. 2 (Figueroa, R.; Froese, R. D.; He, Y.; Klosin, J.; Theriault, C. N.; Abboud, K. A. *Organometallics* **2011**, *30*, 1695-1709, Froese, R. D.; Jazdzewski, B. A.; Klosin, J.; Kuhlman, R. L.; Theriault, C.N.; Welsh, D. M; Abboud, K. A. *Organometallics* **2011**, *30*, 251-262)



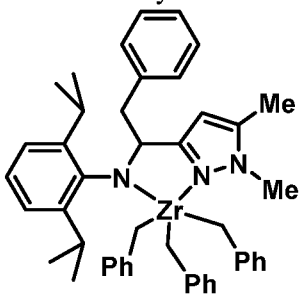
Catalyst 1



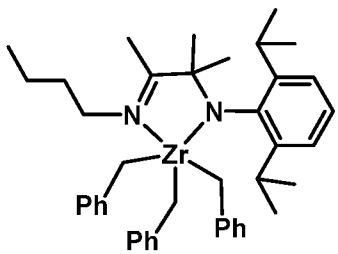
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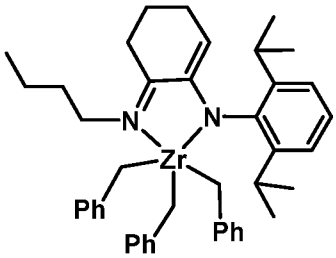
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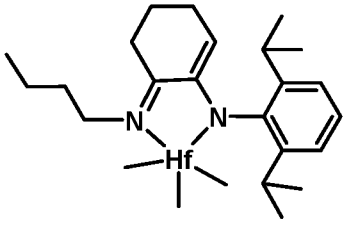
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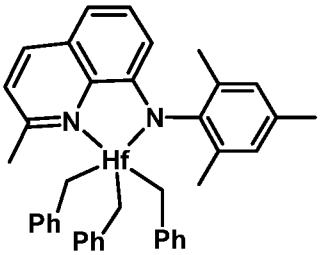
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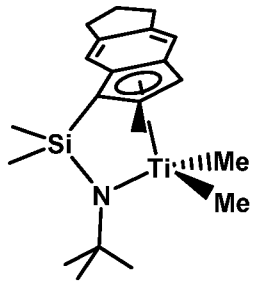
Catalyst 6



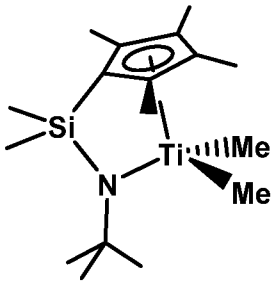
Catalyst 7



Catalyst 8



Comparative Catalyst C1



Comparative Catalyst C2

[00177] The single chain catalyst in Series 3.C (Comp. Cat. C1) incorporated increased amount of α-olefin as indicated by the two-fold and higher octene level in the polymer when compared to the other catalysts. When using the single chain catalyst in Series 3.C ((Comp. Cat. C1) the various levels of added diene had no significant effect on the polymer MWD. However, adding the diene to the dual chain catalysts in Table 3 through Table 7 resulted in higher values of M_w and M_p as diene level was increased, and often there was no evidence of a high molecular weight tail forming.

[00178] In each example contain diene, the amount of diene incorporated into the reactor was small in comparison to the other reactants in the reactor. Therefore, the addition of diene did not affect the amount of comonomer, ethylene, and solvent added into the reactor.

Example 1 –Tetra-functional branching with 3-methyl-1,4-pentadiene

Table 3: Small scale polymerizations (PPR) with 3-methyl-1,4-pentadiene as the diene species.

Ex.	Cat	Cat Added (μmol)	Diene in Octene (vol%)	Octene in Poly (mol%)	Poly Yield (g)	Time (s)	Conventional GPC Data and Metrics						
							Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
							(g/mole)						
3.C.1	Comp. Cat C1	0.020	0	37.4	0.13	1801	3,049	7,138	6,607	1.00	1.00	0.072	0.021
3.C.2			4	35.7	0.14	1801	3,282	7,515	7,079	1.05	1.07	0.057	0.021
3.C.3			6	31.5	0.18	116	3,030	6,883	6,457	0.96	0.98	0.063	0.020
3.1.1	Cat. 1	0.025	0	16.6	0.28	37	6,471	35,214	14,454	1.00	1.00	0.41	0.12
3.1.2			2	15.3	0.24	37	6,608	41,256	15,849	1.17	1.10	0.055	0.069
3.1.3			4	13.4	0.18	43	7,797	53,276	21,878	1.51	1.51	0.12	0.034
3.1.4			6	13.1	0.18	42	9,310	55,406	25,119	1.57	1.74	0.26	0.059
3.4.1	Cat. 2	0.025	0	15.2	0.20	28	5,293	27,847	11,749	1.00	1.00	0.203	0.083
3.4.2			2	12.5	0.18	32	6,921	41,491	17,783	1.49	1.51	-0.29	0.016
3.4.3			4	11.6	0.16	45	8,142	46,098	22,388	1.66	1.91	0.083	0.028
3.4.4			6	12.0	0.17	38	8,333	44,892	21,878	1.61	1.86	0.15	0.037

Example 2 –Tetra-functional branching with 1,4-pentadiene

Table 4: Small scale polymerizations (PPR) with 1,4-pentadiene as the diene species.

Ex.	Cat	Cat Added µmol	Diene in Octene vol%	Octene in Poly mol%	Poly Yield g	Time (s)	Conventional GPC Data and Metrics						
							Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
							(g/mole)						
4.3.1	Cat. 2	0.015	0	12.9	0.17	30	7,330	29,587	16,596	1.00	1.00	0.13	0.033
4.3.2			1	12.6	0.16	40	9,251	46,581	28,184	1.57	1.70	0.39	0.063
4.3.3			2	11.3	0.15	47	12,460	68,277	45,710	2.31	2.75	0.31	0.06
4.3.4			3	9.8	0.15	39	15,999	82,060	53,705	2.77	3.24	0.13	0.057
P2.4.1	Cat. 4	0.020	0	6.3	0.08	112	5,613	18,813	13,804	1.00	1.00	-0.10	0.02
P2.4.2			1	5.9	0.08	202	6,726	22,032	16,218	1.17	1.17	-0.089	0.024
P2.4.3			2	5.6	0.07	254	6,983	24,003	17,783	1.28	1.29	-0.063	0.023
4.4.4			3	5.5	0.07	263	7,815	26,562	20,893	1.41	1.51	0.055	0.031

Table 4: Continued

Ex.	Cat	Cat Added (µmol)	Diene in Octene (vol%)	Octene in Poly (mol%)	Poly Yield (g)	Time (s)	Absolute GPC Data and Metrics						
							Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
							(g/mole)						
4.4.1	Cat. 4	0.020	0	6.3	0.08	112	5,383	18,505	11,220	1.00	1.00	-0.31	0.026
4.4.2			1	5.9	0.08	202	5,752	22,399	15,488	1.21	1.38	0.14	0.035
4.4.3			2	5.6	0.07	254	6,785	26,508	20,418	1.43	1.82	0.23	0.043
4.4.4			3	5.5	0.07	263	6,444	27,369	26,916	1.48	2.40	0.22	0.036

[00179] FIG. 20 illustrates the shift in peak weight average molecular weight as the amount of diene is increased. In FIG. 20, the P2.4.1 – P2.4.4 series, as recorded in Table 4, are plotted as dWdLogM as a function as LogM, which is a GPC plot. As the volume percent of diene increased, the peak in the GPC plot shifted right.

Example 3 –Tetra-functional branching with 1,5-hexadiene

Table 5: Small scale polymerizations (PPR) with 1,5-hexadiene as the diene species.

Ex.	Cat	Cat Added (µmole)	Diene in Octene (vol%)	Octene in Poly (mol%)	Poly Yield (g)	Time (s)	Conventional GPC Data and Metrics						
							Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
							(g/mole)						
5.C.1	Comp Cat. C1	0.020	0	34.3	0.09	1801	3,394	7,576	6,761	1.00	1.00	0.01	0.018
5.C.2			1	34.4	0.11	1802	3,550	7,596	6,457	1.00	0.95	-0.006	0.018
5.C.3			2	35.5	0.10	1801	3,742	8,000	7,244	1.06	1.07	0.011	0.020
5.C.4			3	30.3	0.11	1800	3,509	8,059	7,244	1.06	1.07	0.001	0.021
5.1.1	Cat. 3	0.012	0	7.5	0.09	104	19,503	42,284	38,020	1.00	1.00	0.095	0.025

5.1.2			1	6.3	0.05	1800	22,832	48,933	42,659	1.16	1.12	0.12	0.022
5.1.3			2	8.6	0.06	1801	23,497	51,097	45,710	1.21	1.20	0.11	0.024
5.2.4			3	6.4	0.03	1800	24,880	54,297	48,979	1.28	1.29	0.10	0.024
6.2.1	Cat. 5	0.012	0	6.6	0.08	62	4,345	11,676	10,000	1.00	1.00	0.078	0.021
6.2.2			1	6.3	0.08	81	6,212	15,666	13,183	1.34	1.32	0.065	0.022
6.2.3			2	5.4	0.07	159	9,304	22,290	19,055	1.91	1.91	0.036	0.022
6.2.4			3	8.9	0.07	118	7,337	17,426	15,849	1.49	1.58	-0.007	0.019
6.3.1	Cat. 6	0.015	0	11.6	0.09	120	6,030	18,085	15,488	1.00	1.00	0.012	0.020
6.3.2			1	11.5	0.09	117	6,801	18,582	16,596	1.03	1.07	0.043	0.022
6.3.3			2	9.3	0.07	1103	8,275	24,908	21,380	1.38	1.38	-0.002	0.025
6.3.4			3	10.4	0.09	135	9,283	33,604	28,841	1.86	1.86	0.092	0.028

Example 4 –Tetra-functional branching with 1,7-octadiene

Table 6: Small scale polymerizations (PPR) with 1,7-octadiene as the diene species.

Ex.	Cat	Cat Added (μmole)	Diene in Octene (vol%)	Octene in Poly (mol%)	Poly Yield (g)	Time (s)	Conventional GPC Data and Metrics						
							Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
							(g/mole)						
6.C.1	Comp. Cat. C1	0.020	0	37	0.24	48	1,127	2,230	1,862	1.00	1.00	0.039	0.019
6.C.2			2	38	0.24	51	1,125	2,248	1,905	1.01	1.02	0.006	0.022
6.C.3			4	37	0.23	56	1,124	2,201	1,862	0.99	1.00	0.019	0.020
6.C.4			6	31	0.24	57	1,135	2,352	1,995	1.05	1.07	0.028	0.021
6.3.1	Cat. 6	0.015	0	13	0.10	62	4,825	13,681	12,023	1.00	1.00	0.10	0.024
6.3.2			2	12	0.10	92	5,755	21,647	16,218	1.58	1.35	-0.17	0.023
6.3.3			4	11	0.10	111	6,913	31,963	30,200	2.34	2.51	0.15	0.040
6.3.4			6	10	0.10	125	6,870	54,771	39,812	4.00	3.31	0.19	0.074
6.4.1	Cat. 2	0.015	0	11	0.14	38	12,882	41,563	28,184	1.00	1.00	0.080	0.029
6.4.2			2	11	0.15	34	12,623	61,652	33,885	1.48	1.20	0.36	0.061
6.4.3			4	10	0.14	43	17,699	101,921	47,865	2.45	1.70	0.19	0.094
6.5.1	Cat. 4	0.020	0	6	0.07	131	7,927	20,744	15,849	1.00	1.00	-0.089	0.019
6.5.2			2	6	0.08	234	6,838	22,368	15,488	1.08	0.98	-0.073	0.025
6.5.3			4	6	0.07	267	7,554	24,192	15,488	1.17	0.98	-0.032	0.028
6.5.4			6	5	0.07	353	7,459	25,772	16,218	1.24	1.02	-0.058	0.025

Example 5 –Tetra-functional branching with 1,9-decadiene

Table 7: Small scale polymerizations (PPR) with 1,9-decadiene as the diene species.

Ex.	Cat	Cat Added (μmol)	Diene in Octene (vol%)	Octene in Poly (mol%)	Poly Yield (g)	Time (s)	Conventional GPC Data and Metrics						
							Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
							(g/mole)						
7.1.1	Cat. 3	0.012	0	11	0.13	50	10,690	25,915	20,418	1.00	1.00	0.14	0.027
7.1.2			2	9	0.14	45	10,420	43,497	26,916	1.68	1.32	0.23	0.044
7.1.3			4	7	0.11	52	22,410	93,485	54,956	3.61	2.69	0.29	0.079
7.2.1	Cat. 5	0.012	0	-	0.11	32	2,961	10,454	7,413	1.00	1.00	-0.012	0.024
7.2.2			2	8	0.11	39	4,151	14,343	8,912	1.37	1.20	0.001	0.027
7.2.3			4	8	0.11	32	3,837	16,980	11,220	1.62	1.51	-0.14	0.021
7.2.4			6	6	0.11	32	5,604	22,682	12,883	2.17	1.74	-0.19	0.022
7.3.1	Cat. 6	0.015	0	14	0.11	49	5,141	16,272	14,125	1.00	1.00	0.092	0.026
7.3.2			2	13	0.11	55	6,537	26,292	18,197	1.62	1.29	-0.046	0.033
7.3.3			4	11	0.11	48	8,273	44,729	33,114	2.75	2.34	0.22	0.062
7.3.4			6	11	0.11	68	9,422	93,485	41,688	5.75	2.95	0.31	0.15
7.4.1	Cat. 2	0.015	0	10	0.14	36	14,989	47,160	35,482	1.00	1.00	0.15	0.035
7.4.2			2	10	0.16	33	15,195	87,298	39,812	1.85	1.12	0.027	0.073
7.4.3			4	9	0.14	45	21,234	189,596	56,236	4.02	1.58	-0.44	0.008
7.4.4			6	9	0.16	39	19,657	301,779	48,979	6.40	1.38	-1.65	0.019
7.5.1	Cat. 4	0.020	0	5	0.07	122	9,775	25,249	19,055	1.00	1.00	-0.072	0.020
7.5.2			2	5	0.08	146	8,156	27,499	18,197	1.09	0.95	-0.006	0.030
7.5.3			4	5	0.07	140	9,137	31,407	18,197	1.24	0.95	-0.039	0.026
7.5.4			6	5	0.07	140	7,832	34,706	17,783	1.37	0.93	0.001	0.037

BRANCHED EXAMPLES FROM BATCH REACTOR

[00180] The molecular weight distribution (MWD) curve and DSC of two branched examples were studied and compared to linear samples.

Batch Reactor Example 1

[00181] In Table 8 to Table 12, the polymer characteristic of a comparative linear polymer sample (1C) was compared to branched polymers from a batch reactor. Polymerizations reactions occurred at a temperature of 150 °C, in 555 g of ISOPAR-E™ and a hydrogen pressure (ΔH_2) of 200 psi. The ethylene pressure was held constant at 150 psi in the presences of 0.3 μmole of Catalyst 8, 0.36 μmole of Co-Catalyst A (methyldi(tetradecyl)ammonium tetrakis(pentafluorophenyl)borate), and 10 μmole MMAO-3A.

Table 8: Polymer Characteristics of the batch reactor polymer of Example 1 and the comparative.

Ex.	Diene	Diene Added (g)	Yield (g)	Octene (mol%)	T_m (°C)	Conventional GPC Data and Metrics				
						Mn	Mw	Mp	$G_{(79/29)}$	A_{TAIL}
						(g/mole)				
8.C	none	0.00	8.7	7.4	78.1	18,160	62,030	54,820	0.10	0.026
8.1	1,9-decadiene	0.30	37.1	6.5	80.1	19,740	91,498	66,069	-0.06	0.019

Table 8: Continued

Ex.	Diene	Absolute GPC Data and Metrics					gpcBR
		Mn	Mw	Mp	$G_{(79/29)}$	A_{TAIL}	
		(g/mole)					
8.C	none	21,385	69,811	61,662	0.04	0.022	0.34
8.1	1,9-decadiene	23,947	116,322	79,436	-0.05	0.021	0.56

[00182] FIG. 21 is a conventional molecular weight distribution curve of the polymer in series 8.C (linear) and 8.1 (branched), as determined by GPC. The shape of curve of the branched polymer, series 8.1, is altered in comparison to the linear polymer. Additionally, the peak of the molecular weight curve is shifted to the right.

[00183] FIG. 22 is an absolute molecular weight distribution curve of the polymers in series 8.C (linear) and 8.1 (branched), as determined by GPC.

[00184] FIG. 23 is the extensional viscosity fixture of branched sample is series 8.1.

Table 9: Dynamic Mechanical Spectrum of branched sample 8.1 at 190 °C

Ang freq rad/s	**Storage modulus Pa**	**Loss modulus Pa**	**Complex viscosity Pa.s**	**Tan (delta)**	**Complex modulus Pa**	**Phase angle °**
0.10	1436	2340	27457	1.63	2746	58.5
0.16	2067	3057	23285	1.48	3690	55.9
0.25	2884	3932	19412	1.36	4876	53.7
0.40	3943	5000	15995	1.27	6368	51.7
0.63	5296	6296	13039	1.19	8227	49.9
1.00	6994	7865	10525	1.12	10525	48.4
1.58	9141	9784	8448	1.07	13390	46.9
2.51	11801	12140	6740	1.03	16931	45.8
3.98	15091	15014	5347	0.99	21287	44.9
6.31	19096	18527	4217	0.97	26606	44.1
10.00	24072	22867	3320	0.95	33202	43.5

15.85	30284	28233	2612	0.93	41403	43.0
25.12	38022	34775	2051	0.91	51526	42.4
39.81	47720	42681	1608	0.89	64022	41.8
63.10	59580	51766	1251	0.87	78927	41.0
100.00	74626	62604	974	0.84	97408	40.0

[00185] The Dynamic Mechanical Spectrum of the branched Example 8.1 was measured and the results recorded in Table 9. The viscosity at 0.1 radians/second was calculated to be 27,457 Pa s and the viscosity at 100 radians/second was measured to be 974 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 28.2.

[00186] The elasticity factor m is [((tan ($\delta_{0.1}$) - tan (δ_{100}))*1000)/(0.1-100))]. The tan ($\delta_{0.1}$) is the tangent of the phase angle at 0.1 rad/s and the tan (δ_{100}) is the tangent of the phase angle at 100 rad/s. The tan ($\delta_{0.1}$) of the branched polymer in Example 8.1 was 1.6, and the tan (δ_{100}) of Example 1 was 0.8, which yields an elasticity factor of 7.9 at 190 °C.

Table 10: Dynamic Mechanical Spectrum of the Comparative linear sample 8.C at 190 °C

Ang freq rad/s	**Storage modulus Pa**	**Loss modulus Pa**	**Complex viscosity Pa.s**	**Tan (delta)**	**Complex modulus Pa**	**Phase angle °**
0.10	2	89	892	53.30	89	88.9
0.16	3	141	888	48.95	141	88.8
0.25	5	222	883	46.32	222	88.8
0.40	9	350	880	40.88	350	88.6
0.63	16	552	875	33.93	552	88.3
1.00	33	869	870	26.21	870	87.8
1.58	71	1367	863	19.32	1368	87.0
2.51	150	2138	853	14.23	2143	86.0
3.98	316	3325	839	10.52	3340	84.6
6.31	649	5124	819	7.89	5165	82.8
10.00	1294	7798	790	6.02	7904	80.6
15.85	2502	11700	755	4.68	11964	77.9
25.12	4668	17251	711	3.70	17871	74.9
39.81	8351	24781	657	2.97	26151	71.4
63.10	14314	34669	594	2.42	37508	67.6
100.00	23447	47067	526	2.01	52584	63.5

[00187] The Dynamic Mechanical Spectrum of the comparative 8.C was measured and the results recorded in Table 10. The shear viscosity at 0.1 radians/second was calculated to be 892 Pa s and the shear viscosity at 100 radians/second was measured at 526 Pa s, providing a

rheology ratio ($V_{0.1}/V_{100}$) of 1.7. The tan ($\delta_{0.1}$) of the Comparative linear polymer, 8.C, was 53.3, and the tan (δ_{100}) was 2.0, which yields an elasticity factor of 513.4 at 190 °C.

[00188] The rheology ratio of the linear comparative polymer resin was very low (1.7) when compared to the rheology ratio of branched Example, series 8.1. The increased rheology ratio and the low elasticity factor of the branched Example 1, series 8.1, are indicative of non-linear polymer behavior. Strong shear thinning and elastic behavior often exemplify entangled, long-chain branched polymers.

[00189] FIG. 24 is the melt strength obtained by means of a Rheotens device of the branched Example 1, series 8.1.

Branched Example 2

[00190] In Table 11, branched polyethylene was synthesized where the diene was 1,9-decadiene. The branched polymers were polymerized at a temperature of 150 °C, in 555 g of IsoparE and a hydrogen pressure (ΔH_2) of 200 psi. The ethylene pressure was held constant at 150 psi in the presences of 0.3 µmole of Catalyst 7, 0.36 µmole of Co-Catalyst A, and 10 µmole MMAO-3A.

Table 11: Polymer Characteristics of the branched polymer of Example 2 and the comparative.

Ex.	Diene Amt (g)	Yield (g)	Oct. mol%	T_m (°C)	Conventional GPC Data and Metrics					Absolute GPC Data and Metrics					gpcBR
					Mn	Mw	Mp	$G_{(79/29)}$	A_{TAIL}	Mn	Mw	Mp	$G_{(79/29)}$	A_{TAIL}	
					(g/mole)					(g/mole)					
11.C	0.00	2.7	7.2	81	23,148	61,069	51,286	0.10	0.026	24,297	70,601	58,886	0.02	0.022	0.33
11.1	0.25	52.3	6.8	82	26,464	86,818	48,978	-0.04	0.025	32,257	110,354	63,098	-0.08	0.023	0.55

[00191] FIG. 25 is a conventional molecular weight distribution curve of the polymers in Branched Example 2 in series 11.C (linear) and 11.1 (branched), as determined by GPC. FIG. 26 is an absolute molecular weight distribution curve of the polymer in series 11.C (linear) and 11.1 (branched), as determined by light scattering triple light detector. The shape of curve of the branched polymer, series 11.1, is altered in comparison to the linear polymer.

[00192] FIG. 27 is the extensional viscosity obtained by extensional viscosity fixture of the Branched Example 2 in series 11.1.

Table 12: Dynamic Mechanical Spectrum of branched Example 2, series 11.1 at 190 °C

Ang freq rad/s	Storage modulus Pa	Loss modulus Pa	Complex viscosity Pa.s	Tan (delta)	Complex modulus Pa	Phase angle °
0.10	792	1577	17643	1.99	1764	63.3
0.16	1185	2125	15351	1.79	2433	60.9
0.25	1718	2816	13133	1.64	3299	58.6
0.40	2437	3686	11101	1.51	4419	56.5
0.63	3391	4770	9275	1.41	5852	54.6
1.00	4638	6115	7675	1.32	7675	52.8
1.58	6251	7785	6299	1.25	9984	51.2
2.51	8298	9841	5125	1.19	12873	49.9
3.98	10907	12428	4153	1.14	16535	48.7
6.31	14149	15611	3339	1.10	21069	47.8
10.00	18216	19588	2675	1.08	26749	47.1
15.85	23370	24603	2141	1.05	33933	46.5
25.12	29874	30846	1710	1.03	42941	45.9
39.81	38172	38601	1364	1.01	54288	45.3
63.10	48558	47806	1080	0.98	68142	44.6
100.00	62045	59123	857	0.95	85704	43.6

[00193] The Dynamic Mechanical Spectrum of the comparative was measured and the results recorded in Table 12. The shear viscosity at 0.1 radians/second was calculated to be 17,643 Pa s and the shear viscosity at 100 radians/second was measured at 857 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 20.6. The tan ($\delta_{0.1}$) of the branched polymer in Example 2, series 11.1, was 2.0, and the tan (δ_{100}) was 1.0, which yields an elasticity factor of 10.4 at 190 °C.

[00194] FIG. 28 is the melt strength obtained by a Rheotens device of the Branched Example 2, series 11.1.

BRANCHING STUDY UNDER VARIOUS CONDITIONS

[00195] The tetra-functional "Ladder Branching" was studied under various conditions, such as increased ethylene pressure, increased octene monomer, increased starting molecular weight, decreased starting molecular weight, various dienes, increased or decreased diene amounts, and various multi-chain catalysts.

Example 1: Various Dienes and Amounts of Dienes

[00196] The examples in Table 13 to Table 22 were prepared under identical conditions and polymerized in the presence of Catalyst 7 at a temperature of 150 °C. The conditions included: 585 g IsoparE; 15 g 1-octene; hydrogen pressure of 240 psi; ethylene pressure of 150 psi; 0.3 μmole of Catalyst 7; 0.36 μmole Co-Catalyst A; and 10 μmole MMAO-3A.

Table 13. Various dienes tested under identical conditions with Catalyst 7

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Oct. Poly mol%	T_m (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mw_o	Mp / Mp_o	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
13C	none	0.00	8.5	3.4%	109.8	21,059	64,711	51,286	1.00	1.00	0.095	0.027
13.1	1,3-divinylcyclopentane	0.70	5.6	3.0%	110.4	22,523	71,923	58,884	1.11	1.15	0.11	0.027
13.2	1,4-hexadiene	0.35	7.8	2.9%	112.2	22,400	72,446	52,481	1.12	1.02	0.088	0.027
13.3	1,4-hexadiene	0.75	6.0	2.6%	115.3	22,014	78,338	56,234	1.21	1.10	0.036	0.025
13.4	2-me-hexadiene	0.50	4.1	3.2%	109.6	26,792	83,247	69,183	1.29	1.35	0.11	0.026
13.5	2-me-pentadiene	0.25	8.0	3.0%	110.4	21,430	66,827	50,119	1.03	0.98	0.13	0.030
13.6	2-me-pentadiene	0.45	10.5	3.1%	110.8	22,180	65,274	51,286	1.01	1.00	0.14	0.030
13.7	2-me-pentadiene	0.50	7.0	2.9%	110.2	21,443	72,911	53,703	1.13	1.05	0.11	0.030
13.8	2-me-pentadiene	1.00	4.7	2.8%	111.6	20,601	75,340	56,234	1.16	1.10	0.077	0.027
13.9	3-me-pentadiene	0.25	9.5	3.0%	111.5	22,882	74,859	52,481	1.16	1.02	0.16	0.032
13.10	3-me-pentadiene	0.50	9.8	3.2%	111.3	22,261	77,008	50,119	1.19	0.98	0.078	0.027
13.11	1,9-decadiene	0.20	7.4	2.8%	111.2	27,008	100,136	52,481	1.55	1.02	-0.10	0.023
13.12	1,9-decadiene	0.25	7.7	2.6%	115.4	27,458	124,092	63,096	1.92	1.23	-0.27	0.023
13.13	1,9-decadiene	0.30	8.0	2.7%	112.9	28,140	125,235	58,884	1.94	1.15	-0.13	0.029
13.14	1,9-decadiene	0.50	11.3	3.0%	114.2	22,091	174,694	134,896	2.70	2.63	0.031	0.055
13.15	1,5-hexadiene	0.75	9.6	3.3%	109.9	22,027	77,375	52,481	1.20	1.02	0.10	0.029
13.16	1,8-nonadiene	0.10	7.9	3.2%	110.2	25,803	91,031	57,544	1.41	1.12	0.007	0.024
13.17	1,8-nonadiene	0.20	6.4	3.4%	108.1	27,604	114,480	81,283	1.77	1.58	-0.092	0.019
13.18	1,8-nonadiene	0.30	3.5	2.9%	104.8	31,057	147,084	120,226	2.27	2.34	-0.14	0.031
13.19	1,7-	0.16	9.0	2.9%	111.2	26,018	86,041	52,481	1.33	1.02	0.14	0.033

	octadiene											
13.20	1,7-octadiene	0.24	9.1	2.7%	112.6	26,711	96,007	53,703	1.48	1.05	-0.002	0.026
13.21	1,7-octadiene	0.30	7.3	2.6%	113.3	28,484	104,803	57,544	1.62	1.12	-0.14	0.018
13.22	1,7-octadiene	0.35	8.9	2.8%	112.8	24,548	110,395	58,884	1.71	1.15	-0.15	0.019
13.23	1,4-pentadiene	0.10	7.4	3.7%	111.3	19,698	81,929	64,565	1.27	1.26	0.16	0.033
13.24	1,4-pentadiene	0.20	1.9	3.0%	105.1	31,887	101,861	67,608	1.57	1.32	-0.11	0.013
13.25	1,4-pentadiene	0.30	1.1	2.3%	108.7	29,809	107,172	69,183	1.66	1.35	-0.21	0.013

Table 13: Continued

Ex.	Absolute GPC Data and Metrics							$V_{0.1}/V_{100}$	m	gpcBR
	Mn	Mw	Mp	Mw / Mw_o	Mp / Mp_o	$G_{(79/29)}$	A_{TAIL}			
	(g/mole)									
13C	25,552	67,491	60,258	1.00	1.00	0.021	0.020	1.5	768	0.18
13.12	36,181	159,527	67,611	2.36	1.12	0.018	0.041	121.4	0.412	0.56
13.16	31,935	105,263	67,611	1.56	1.12	0.082	0.032	28.2	6.338	0.35
13.17	38,628	143,672	97,728	2.13	1.62	0.066	0.027	110.4	1.025	0.51
13.18	42,764	198,061	128,832	2.93	2.14	0.043	0.041	--		0.70
13.22	33,516	138,854	70,797	2.06	1.17	0.048	0.037	101.4	1.018	0.52

[00197] The results in Table 13 indicated that when diene was present in the polymerization reaction, molecular weight increased without a high molecular weight tail.

Example 2: Conditions that yield high molecular weights

Table 14: Nonadiene tested under conditions giving a higher linear MW

Ex.	Diene	Diene Amt (g)	Poly Yield (g)	Octene in Poly (mol%)	T_m (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mw_o	Mp / Mp_o	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
14.C	none	0	12.4	3.2	109.5	31,796	93,455	70,795	1.00	1.00	0.13	0.027
14.1	1,8-nonadiene	0.2	6.9	2.9	106.4	46,835	211,514	141,254	2.26	2.00	0.03	0.031
14.2	1,8-nonadiene	0.5	3.5	2.8	107.1	52,396	387,644	288,403	4.15	4.07	0.59	0.110

T=150 °C, IsoparE: 585g, 1-octene: 15 g; ΔH_2: 140 psi, Ethylene: 150 psi, Catalyst 7: 0.3 μmole, Co-Catalyst A: 0.36 μmole, MMAO-3A: 10 μmole.

[00198] Utilizing those polymerization conditions to produce high molecular weight polymers resulted in tetra-functional "Ladder Branching", which occurred when the diene was incorporated into the polymerization reaction. The polymerization reaction yielded polymer resins with high molecular weights and tetra-functional "Ladder Branching".

Example 3: Conditions that yield branched homopolymer

Table 15: High density polyethylene examples using decadiene and pentadiene

Ex.	Diene	Diene Added (g)	Poly Yield (g)	T_m (°C)	Conventional GPC Data and Metrics						
					Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
					(g/mole)						
15.C	0	0.00	7.1	133.2	18,988	60,271	50,119	1.00	1.00	0.12	0.028
15.1	1,9-decadiene	0.15	7.0	135.0	23,754	102,744	58,884	1.70	1.17	0.04	0.033
15.2	1,4-pentadiene	0.1	2.3	133.9	22,525	104,216	70,795	1.73	1.41	-0.06	0.013
15.3	1,4-pentadiene	0.2	1.3	135.1	28,186	114,916	81,283	1.91	1.62	-0.23	0.015

T=160 °C, IsoparE: 600g, 1-octene: 0 g; ΔH_2: 240 psi, Ethylene: 150 psi, Catalyst 7: 0.4 µmole, Co-Catalyst A: 0.48 µmole, MMAO-3A: 10 µmole.

[00199] Incorporating diene into the polymerization reaction used to make homopolymers (with a small amount of diene) resulted in an increase in molecular weight (tetra-functional "Ladder Branching"). The data recorded in Table 15 indicated that the examples of ethylene only resins increased in molecular weight when two different dienes where incorporated into the polymerization reaction.

Table 16: Lower density polyethylene examples using pentadiene with Catalyst 8

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Octene in Poly (mol%)	T_m (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mw_o	Mp / Mp_o	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
16.C	none	0	3.4	7.0	79.5	21,739	65,347	53,703	1.00	1.00	0.12	0.028
16.1	1,4-pentadiene	0.1	1.4	7.3	81.2	23,203	75,022	57,544	1.15	1.07	0.14	0.031
16.2	1,4-pentadiene	0.2	1.9	7.0	81.2	25,701	84,942	60,256	1.30	1.12	0.06	0.024

T=150 °C, IsoparE: 555g, 1-octene: 45 g; ΔH_2: 220 psi, Ethylene: 150 psi, Catalyst 8: 0.4 µmole, Co-Catalyst A: 0.48 µmole, MMAO-3A: 10 µmole.

[00200] The results in Table 16 indicated that branching occurs with different catalysts and at different densities. The resins in Table 16 demonstrated branching with Catalyst 8 and enough octene for 7 mol% in the polymer.

Table 17: Lower density polyethylene examples using pentadiene and decadiene at higher linear MW with Catalyst 8

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Oct. mol%	T_m (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
17.C	none	0.00	5.4	-	85.1	31,155	100,236	79,433	1.00	1.00	0.10	0.024
17.1	1,9-decadiene	0.30	5.6	-	82.0	28,449	143,906	104,713	1.44	1.32	-0.66	0.021
17.2	1,4-pentadiene	0.20	2.0	-	84.5	33,901	141,038	100,000	1.41	1.26	-0.76	0.014

T=150 °C, IsoparE: 555g, 1-octene: 45 g; ΔH_2: 140 psi, Ethylene: 150 psi, Catalyst 8: 0.3 µmole, Co-Catalyst A: 0.36 µmole, MMAO-3A: 10 µmole.

[00201] Based on the results in Table 17, molecular weight increased with addition of diene indicative of tetra-functional "Ladder Branching". These examples had higher linear molecular weights. In examples 5.1 and 5.2, Catalyst 8 produced polymer resins with a higher molecular weight when decadiene or pentadiene was present in the polymerization reactions.

Table 18: Hexene used as a comonomer in place of octene and comparing different catalysts with decadiene

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Hexene in Poly (mol%)	Tm (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
18.1.C*	none	0	11.5	2.4	114.3	21,627	61,061	47,863	1.00	1.00	0.13	0.029
18.1.1*	1,9-decadiene	0.35	5.2	2.4	117.1	24,307	132,150	93,325	2.16	1.95	-0.12	0.036
18.2.C**	none	0	7.9	5.6	103.5	17,419	58,044	50,119	1.00	1.00	0.09	0.026
18.2.1**	1,9-decadiene	0.25	4.0	5.5	92.2	22,482	96,617	70,795	1.66	1.41	-0.03	0.021

T=150 °C, Ethylene: 150 psi, MMAO-3A: 10 µmole,
*IsoparE: 585g, 1-hexene: 15 g; ΔH_2: 240 psi, Catalyst 7: 0.3 µmole, Co-Catalyst A: 0.36 µmole.
** IsoparE: 555g, 1-hexene: 45 g; ΔH_2: 200 psi, Catalyst 8: 0.3 µmole, Co-Catalyst A: 0.36 µmole.

[00202] The results in Table 18 indicated that increases in molecular weight (tetra-functional "Ladder Branching") occurred when a different α-olefin comonomer was used. The polymer resins in Table 18 were produced by two different catalysts and two different loadings of hexene.

Table 19: Lower density polyethylene examples using decadiene at higher linear MW with Catalyst 7

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Octene in Poly (mol%)	Tm (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
19.C	None	0.00	8.5	7.1	78.1	37,359	102,362	77,625	1.00	1.00	0.12	0.026
19.1	1,9-decadiene	0.15	4.9	5.0	84.2	30,255	159,937	87,096	1.56	1.12	-1.44	0.017
19.2	1,9-decadiene	0.30	9.0	6.9	80.4	45,031	194,779	109,648	1.90	1.41	-0.26	0.031

T=150 °C, IsoparE: 555g, 1-octene: 45 g; ΔH_2: 60 psi, Ethylene: 150 psi, Catalyst 7: 0.3 µmole, Co-Catalyst A: 0.36 µmole, MMAO-3A: 10 µmole.

[00203] Based on the results in Table 19, increases in molecular weight with diene (tetra-functional "Ladder Branching") occurred with different levels of octene. The examples in Table

19 indicated that even with 7 mol% octene in the polymer, tetra-functional "Ladder Branching" occurred.

Table 20: Branching with different dienes such as pentadiene

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Octene in Poly (mol%)	Tm (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
20.C	none	0.00	6.3	7.5	77.1	29,605	83,716	64,565	1.00	1.00	0.12	0.028
20.1	1,9-decadiene	0.30	7.0	5.0	81.3	35,781	160,761	85,114	1.92	1.32	-0.72	0.028
20.2	1,4-pentadiene	0.20	2.3	4.8	85.3	24,397	132,720	87,096	1.59	1.35	-0.54	0.012

T=150 °C, IsoparE: 555g, 1-octene: 45 g; ΔH_2: 100 psi, Ethylene: 150 psi, Catalyst 7: 0.3 µmole, Co-Catalyst A: 0.36 µmole, MMAO-3A: 10 µmole.

[00204] As evidenced in Table 20, tetra-functional "Ladder Branching" occurred with different levels of octene and higher starting molecular weights. The examples 8.1 and 8.2 indicated that a polymer resin with 7 mol% octene and starting M_w of approximately 83,000 g/mol led to branching both with decadiene and pentadiene.

Table 21: Branching with high levels of octene and low linear molecular weights.

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Octene in Poly (mol%)	Tm (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
21.C	none	0.00	12.8	9.6	69.6	15,073	43,074	38,019	1.00	1.00	0.15	0.028
21.1	1,9-decadiene	0.45	4.2	9.0	74.1	18,788	82,682	50,119	1.92	1.32	-0.03	0.029

T=150 °C, IsoparE: 542g, 1-octene: 58 g; ΔH_2: 200 psi, Ethylene: 150 psi, Catalyst 7: 0.3 µmole, Co-Catalyst A: 0.36 µmole, MMAO-3A: 10 µmole.

[00205] The results in Table 21 showed there was an increase in molecular weight (tetra-functional "Ladder Branching") at much lower density (high levels of octene in polymer) and lower starting molecular weight. In example 9.1, the polymer resin had greater than 9 mol% octene and starting M_w of approximately 43,000 g/mol. When diene was incorporated into the polymerization reaction, molecular weight increased ("Ladder Branching" occurred).

Table 22: "Ladder Branching" with decadiene at lower linear molecular weights

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Octene in Poly (mol%)	Tm (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
22.C	none	0.00	9.5	7.4	81.5	17,778	51,211	42,658	1.00	1.00	0.13	0.027
22.1	1,9-decadiene	0.25	8.9	7.7	77.9	18,228	70,134	43,652	1.37	1.02	-0.03	0.027

T=150 °C, IsoparE: 555g, 1-octene: 45 g; ΔH_2: 180 psi, Ethylene: 150 psi, Catalyst 7: 0.3 µmole, Co-Catalyst A: 0.36 µmole, MMAO-3A: 10 µmole.

[00206] The results in Table 22 indicated that molecular weight incased with diene (tetra-functional "Ladder Branching") with a different level of incorporated octene at a lower starting molecular weight. In example 22.1, the starting molecular weight of the polymer resin was approximately 51,000 g/mol, and when diene was incorporated into the polymerization reactions, the molecular weight increased to 70,000 g/mol (tetra-functional "Ladder Branching" occurred).

Table 23: Different ethylene pressure and octene added to the reactor

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Octene in Poly (mol%)	Tm (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
23.C	none	0.00	10.0	6.6	83.4	28,232	82,570	66,069	1.00	1.00	0.10	0.026
23.1	1,9-decadiene	0.38	9.5	6.6	83.1	30,603	119,347	70,795	1.45	1.07	-0.20	0.014

T=150 °C, IsoparE: 533g, 1-octene: 67 g; ΔH_2: 240 psi, Ethylene: 233 psi, Catalyst 7: 0.3 µmole, Co-Catalyst A: 0.36 µmole, MMAO-3A: 10 µmole.

[00207] According to the data in Table 23 and Table 24, molecular weights increased (tetra-functional "Ladder Branching" occurred) when the ethylene pressure and amount of octene in the reactor was increased.

Table 24: Varied ethylene pressure and amount of octene added to the reactor.

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Octene in Poly (mol%)	Tm (°C)	Conventional GPC Data and Metrics						
						Mn	Mw	Mp	Mw / Mwo	Mp / Mpo	$G_{(79/29)}$	A_{TAIL}
						(g/mole)						
24.C	none	0.00	10.7	6.0	90.6	47,020	128,732	102,329	1.00	1.00	-0.01	0.016
24.1	1,9-decadiene	0.50	10.4	5.9	88.7	46,782	182,025	112,202	1.41	1.10	-1.07	0.018

T=150 °C, IsoparE: 510g, 1-octene: 90 g; ΔH_2: 240 psi, Ethylene: 300 psi, Catalyst 7: 0.3 µmole, Co-Catalyst A: 0.36 µmole, MMAO-3A: 10 µmole.

Example 4: Catalyst 7 catalyzed decadiene-homopolymer

Table 25: No octene added to the reactor.

Ex.	Diene	Diene Added (g)	Poly Yield (g)	Tm (°C)	Conventional GPC Data and Metrics				
					Mn	Mw	Mp	$G_{(79/29)}$	A_{TAIL}
					(g/mole)				
25.C.1	none	0.00	8.1	133.1	24,817	71,529	63,096	0.07	0.023
25.C.2	none	0.00	8.4	134.9	23,596	68,706	60,256	0.06	0.022

25.1	1,9-decadiene	0.03	8.3	138	27,636	84,420	63,096	0.11	0.027
25.2	1,9-decadiene	0.06	8.5	137.7	26,305	94,520	67,608	-0.01	0.023
25.3	1,9-decadiene	0.10	8.6	138.5	27,549	106,799	75,858	-0.06	0.019
25.4	1,9-decadiene	0.20	8.2	138.7	31,246	149,195	120,226	0.03	0.038

Table 25: Continued

Ex.	Diene	Diene Added (g)	Absolute GPC Data and Metrics					
			Mn	Mw	Mp	$G_{(79/29)}$	A_{TAIL}	gpcBR
			(g/mole)					
25.C.1	none	0.00						
25.C.2	none	0.00	18,771	60,641	47,865	0.06	0.027	0.07
25.1	1,9-decadiene	0.03	21,119	81,512	52,483	0.12	0.035	0.17
25.2	1,9-decadiene	0.06	26,147	97,809	51,288	0.07	0.035	0.25
25.3	1,9-decadiene	0.10	20,182	116,859	66,072	0.04	0.031	0.34
25.4	1,9-decadiene	0.20	29,735	242,736	109,653	0.14	0.075	0.92

T=150 °C, IsoparE: 600g, 1-Octene: 0g (except Entry 25.C.1 which has 0.2 g), ΔH_2: 240 psi, Ethylene: 150 psi, Catalyst 7: 0.4 µmole, Co-Catalyst A: 0.48 µmole, MMAO-3A: 10 µmole.

[00208] Results summarized in Table 25 indicate that tetra-functional "Ladder Branching" occurs when octene is not present in the reactor. The molecular weight of each example in Table 25 increased as the amount of decadiene in the polymerization reaction increased.

Table 26: Carbon and proton NMR evaluation of methines, vinyls, and vinylenes (per 1000 carbon atoms) of the Examples recorded in Table 25.

Example	Octene (g)	Decadiene (g)	methines per 1000 C	Vinyls per 1000 C	Vinylenes per 1000 C
26.C.1	0.2	0.00	0.38	0.04	0
26.C.2	0.0	0.00	0	0.041	0
26.1	0.0	0.03	0.08	0.056	0
26.2	0.0	0.06	0.22	0.085	0.002
26.3	0.0	0.10	0.3	0.12	0.003
26.4	0.0	0.20	0.45	0.2	0.005

[00209] Example 26.C.1 is the result of a polymerization reaction containing 0.2 octene. FIG. 29 is a graph of the Log(MW) of the Examples 26.C.1, 26.C.2, and 26.1 – 26.4. As the amount of decadiene increases, the molecular weight peak shifts right. Table 27 to Table 32 summarize the results of a Dynamic Mechanical Spectrum for Examples 26.C.1, 26.C.2, and 26.1-26.4. The results of each Table 27 to Table 32 indicate the elasticity factor, m, decreases as the amount of tetra-functional "Ladder Branching" increases. Additionally, the results of each Table 27 to

Table 32 indicate the rheology ratio increases as the amount of tetra-functional "Ladder Branching" increases.

[00210] FIG. 29 is a conventional molecular weight distribution of curve of series 26.C.1, 26.C.2, and 26.1 to 26.4.

Table 27: Dynamic Mechanical Spectrum of Example 26.C.1, a linear short chain branched polymer, at 190 °C.

Ang freq rad/s	Storage modulus Pa	Loss modulus Pa	Complex viscosity Pa.s	Tan (delta)	Complex modulus Pa	Phase angle °
0.10	0	76	762	192.81	76	89.7
0.16	1	121	761	145.80	121	89.6
0.25	1	191	760	131.04	191	89.6
0.40	4	302	758	74.41	302	89.2
0.63	9	477	755	55.57	477	89.0
1.00	18	753	753	42.51	753	88.7
1.58	38	1186	749	31.35	1187	88.2
2.51	81	1865	743	22.98	1866	87.5
3.98	170	2922	735	17.22	2927	86.7
6.31	351	4561	725	13.00	4575	85.6
10.00	718	7078	711	9.86	7115	84.2
15.85	1448	10894	693	7.52	10989	82.4
25.12	2865	16568	669	5.78	16814	80.2
39.81	5513	24807	638	4.50	25412	77.5
63.10	10265	36398	599	3.55	37818	74.3
100.00	18369	52036	552	2.83	55183	70.6

[00211] The Dynamic Mechanical Spectrum of the comparative was measured and the results recorded in Table 27. The shear viscosity at 0.1 radians/second was calculated to be 762 Pa s and the shear viscosity at 100 radians/second was measured at 552 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 1.4. The tan ($\delta_{0.1}$) of the branched polymer in Example 26.C.1 was 192.8, and the tan (δ_{100}) was 2.8, which yields an elasticity factor of 1901.6 at 190 °C.

Table 28: Dynamic Mechanical Spectrum of Example 26.C.2, a linear polymer, at 190 °C.

Ang freq rad/s	Storage modulus Pa	Loss modulus Pa	Complex viscosity Pa.s	Tan (delta)	Complex modulus Pa	Phase angle °
0.10	0	66	662	401.31	66	89.9
0.16	0	105	662	212.34	105	89.7
0.25	1	166	661	126.46	166	89.5

0.40	3	263	661	91.50	263	89.4
0.63	6	416	659	70.63	416	89.2
1.00	13	658	658	51.74	658	88.9
1.58	28	1038	655	37.74	1039	88.5
2.51	60	1635	651	27.25	1636	87.9
3.98	127	2567	646	20.19	2570	87.2
6.31	267	4018	638	15.07	4027	86.2
10.00	553	6256	628	11.31	6281	84.9
15.85	1131	9671	614	8.55	9737	83.3
25.12	2272	14793	596	6.51	14967	81.3
39.81	4439	22291	571	5.02	22729	78.7
63.10	8445	32969	539	3.90	34034	75.6
100.00	15436	47687	501	3.09	50123	72.1

[00212] The Dynamic Mechanical Spectrum of the comparative, Example 26.C.1, was measured and the results recorded in Table 28. The shear viscosity at 0.1 radians/second was calculated to be 662 Pa s and the shear viscosity at 100 radians/second was measured at 501 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 1.3. The tan ($\delta_{0.1}$) of the linear polymer of Example 26.C.1 was 401.3, and the tan (δ_{100}) was 3.1, which yields an elasticity factor of 3986.2 at 190 °C.

Table 29: Dynamic Mechanical Spectrum of Example 26.1, a tetra-functional "Ladder Branched" polymer, at 190 °C.

Ang freq rad/s	Storage modulus Pa	Loss modulus Pa	Complex viscosity Pa.s	Tan (delta)	Complex modulus Pa	Phase angle °
0.10	168	722	7410	4.29	741	76.9
0.16	293	1054	6900	3.60	1094	74.5
0.25	492	1514	6336	3.08	1591	72.0
0.40	797	2138	5731	2.68	2282	69.6
0.63	1250	2973	5112	2.38	3225	67.2
1.00	1900	4082	4502	2.15	4502	65.0
1.58	2810	5540	3919	1.97	6211	63.1
2.51	4059	7449	3377	1.84	8483	61.4
3.98	5741	9964	2888	1.74	11499	60.0
6.31	7995	13287	2458	1.66	15507	59.0
10.00	11019	17695	2085	1.61	20845	58.1
15.85	15100	23534	1764	1.56	27961	57.3
25.12	20749	31208	1492	1.50	37476	56.4
39.81	28424	41229	1258	1.45	50078	55.4
63.10	39014	54069	1057	1.39	66675	54.2
100.00	53608	70156	883	1.31	88294	52.6

[00213] The Dynamic Mechanical Spectrum of Example 26.1 was measured and the results recorded in Table 29. The shear viscosity at 0.1 radians/second was calculated to be 7,410 Pa s and the shear viscosity at 100 radians/second was measured at 883 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 8.4. The tan ($\delta_{0.1}$) of the branched polymer in Example 13.1 was 4.3, and the tan (δ_{100}) was 1.3, which yields an elasticity factor of 29.8 at 190 °C.

Table 30: Dynamic Mechanical Spectrum of Example 26.2, a tetra-functional "Ladder Branched" polymer, at 190 °C.

Ang freq rad/s	Storage modulus Pa	Loss modulus Pa	Complex viscosity Pa.s	Tan (delta)	Complex modulus Pa	Phase angle °
0.10	3624	4341	56549	1.20	5655	50.1
0.16	4876	5401	45910	1.11	7276	47.9
0.25	6427	6657	36837	1.04	9253	46.0
0.40	8332	8102	29193	0.97	11622	44.2
0.63	10654	9784	22926	0.92	14465	42.6
1.00	13448	11749	17858	0.87	17858	41.1
1.58	16769	14037	13798	0.84	21869	39.9
2.51	20720	16721	10600	0.81	26626	38.9
3.98	25363	19928	8102	0.79	32255	38.2
6.31	30848	23813	6176	0.77	38969	37.7
10.00	37319	28572	4700	0.77	47001	37.4
15.85	45028	34475	3578	0.77	56711	37.4
25.12	54324	41765	2728	0.77	68524	37.6
39.81	65674	50951	2088	0.78	83121	37.8
63.10	79710	62296	1603	0.78	101170	38.0
100.00	97327	76112	1236	0.78	123550	38.0

[00214] The Dynamic Mechanical Spectrum of Example 26.2 was measured and the results recorded in Table 30. The shear viscosity at 0.1 radians/second was calculated to be 56,549 Pa s and the shear viscosity at 100 radians/second was measured at 1,236 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 45.8. The tan ($\delta_{0.1}$) of the branched polymer in Example 26.2 was 1.2, and the tan (δ_{100}) was 0.8, which yields an elasticity factor of 4.2 at 190 °C.

Table 31: Dynamic Mechanical Spectrum of Example 26.3, a tetra-functional "Ladder Branched" polymer, at 190 °C.

Ang freq rad/s	Storage modulus Pa	Loss modulus Pa	Complex viscosity Pa.s	Tan (delta)	Complex modulus Pa	Phase angle °
0.10	17977	12228	217410	0.68	21741	34.2
0.16	21869	13969	163730	0.64	25950	32.6

0.25	26179	15829	121790	0.60	30592	31.2
0.40	31006	17912	89945	0.58	35808	30.0
0.63	36358	20148	65880	0.55	41567	29.0
1.00	42361	22662	48042	0.53	48042	28.1
1.58	49016	25437	34844	0.52	55223	27.4
2.51	56469	28527	25187	0.51	63266	26.8
3.98	64746	32041	18146	0.49	72241	26.3
6.31	73992	36161	13052	0.49	82355	26.0
10.00	84312	41035	9377	0.49	93767	26.0
15.85	95926	46900	6737	0.49	106780	26.1
25.12	109110	54015	4847	0.50	121750	26.3
39.81	124270	62740	3497	0.50	139210	26.8
63.10	142000	73445	2534	0.52	159870	27.3
100.00	163090	86354	1845	0.53	184540	27.9

[00215] The Dynamic Mechanical Spectrum Example 26.3 was measured and the results recorded in Table 31. The shear viscosity at 0.1 radians/second was calculated to be 56,549 Pa s and the shear viscosity at 100 radians/second was measured at 1,236 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 117.8. The tan ($\delta_{0.1}$) of the branched polymer in Example 26.3 was 1.2, and the tan (δ_{100}) was 0.8, which yields an elasticity factor of 4.2 at 190 °C.

Table 32: Dynamic Mechanical Spectrum of Example 26.4, a tetra-functional "Ladder Branched" polymer, at 190 °C.

Ang freq rad/s	Storage modulus Pa	Loss modulus Pa	Complex viscosity Pa.s	Tan (delta)	Complex modulus Pa	Phase angle °
0.10	86332	28452	909000	0.33	90900	18.2
0.16	95178	30306	630240	0.32	99887	17.7
0.25	104510	32167	435310	0.31	109340	17.1
0.40	114280	34156	299610	0.30	119280	16.6
0.63	124490	36260	205500	0.29	129660	16.2
1.00	135390	38643	140790	0.29	140790	15.9
1.58	146880	41177	96245	0.28	152540	15.7
2.51	159050	43788	65676	0.28	164970	15.4
3.98	172020	46770	44777	0.27	178260	15.2
6.31	185770	50056	30493	0.27	192400	15.1
10.00	200450	53794	20754	0.27	207540	15.0
15.85	216100	58080	14119	0.27	223770	15.0
25.12	232940	63088	9607	0.27	241330	15.2
39.81	251110	69110	6542	0.28	260440	15.4
63.10	270990	76373	4462	0.28	281550	15.7
100.00	293290	85175	3054	0.29	305410	16.2

[00216] The Dynamic Mechanical Spectrum of Example 26.4 was measured and the results recorded in Table 32. The shear viscosity at 0.1 radians/second was calculated to be 909,000 Pa s and the shear viscosity at 100 radians/second was measured at 3,054 Pa s, providing a rheology ratio ($V_{0.1}/V_{100}$) of 297.6. The tan ($\delta_{0.1}$) of the branched polymer in Example 26.4 was 0.3, and the tan (δ_{100}) was 0.3, which yields an elasticity factor of 0.4 at 190 °C.

[00217] Guzman-2010 demonstrated and analyzed the MWD and physical properties resulting from conventional diene branching in a steady-state CSTR. A constrained geometry catalyst (CGC) was used to copolymerize ethylene, 1-octene, and 1,9-decadiene in a very well mixed one-gallon reactor system. The particular CGC catalyst, used by Guzman, was described in detail by U.S. Pat. No. 5,965,756 (structure IX) and U.S. Pat. No. 7,553,917 (Example 3). The Guzman-2010 catalyst was designed to grow a single chain from the catalyst center. Guzman's data were gathered at steady state while operating a CSTR at a pressure of 525 psig and a temperature of 155 °C over a range of diene feed concentrations. The various steady-state polymer samples collected by Guzman contained no measurable levels of gels or insoluble material. However, at the highest level of dienes feed some minor internal reactor fouling was observed, and it was anticipated that higher levels of dienes feed would result in gels formation or reactor MWD instability.

[00218] In Table 33, a selected series of data from Guzman was summarized for otherwise fixed reactor conditions over a spectrum of diene feed levels. Throughout the series, the ethylene and 1-octene feed concentrations were set at 13.8 wt% and 3.6 wt%, respectively. The catalyst feed rate was continuously adjusted to maintain a constant ethylene conversion of 79% throughout the series resulting in a fixed polymer production rate of 2.2 kg/hr. The polymer density, a measure of copolymer composition, was constant at about 0.922 g/cc.

Table 33: Comparative example of Guzman CSTR results using a single-chain constrained geometry catalyst and 1,9-decadiene.

Sample	1,9-decadiene		vinyls/ 1000C	I_2 (dg/min)	I_{10}/I_2	Conventional GPC Data			Absolute GPC Data		
	Feed (ppm)[A]	Incorp. (ppm)[B]				M_n	M_w	M_p	M_n	M_w	M_p
						(kg/mole)			(kg/mole)		
33.C1	0	0	0.11	20	6.2	19.9	42.5	35.8	21.5	48.2	39.1
33.C2	523	2119	0.25	7.2	9.1	19.4	52.9	36.5	20.2	58.9	38.6
33.C3	704	2912	0.29	4.6	10.2	19.5	55.5	37.4	21.4	67.2	39.1
33.C4	794	3186	0.30	3.2	11.0	20.9	59.5	36.4	22.5	73.6	39.0
33.C5	837	3405	0.30	3.1	11.5	20.2	60.2	36.9	21.7	75.3	38.5
33.C6	881	3502	0.28	2.1	11.8	21.6	65.2	38.9	23.0	81.5	41.9

33.C7	923	3946	0.31	1.3	13.0	21.9	70.4	40.8	23.9	90.4	39.9

A. 1,9-decadiene feed level expressed as overall mass fraction, in units of ppm
B. 1,9-decadiene incorporation as expressed in polymer mass fraction, in units of ppm.

[00219] The data in Table 33 demonstrated how changes in conventional diene branching level affects average molecular weight and polydispersity as well as properties such as viscosity, as reflected by I_2 and I_{10}. The effect of conventional diene branching on molecular weight was shown in Table 33 for both absolute and conventional MWD measurement techniques. While absolute MWD measurement is the preferred method for branched polymers, it is not always available. Therefore, Table 33 also contains molecular weights measured by conventional techniques using a refractive index detector. The results in Table 33 demonstrated that, by either measurement technique, the weight average molecular weight (M_w) rises substantially as the diene feed is increased from zero to 923 ppm.

[00220] Though not reported in Guzman, the MWD curves associated with Table 33 were found and plotted in FIGS. 30A and 30B for absolute and conventional GPC measurement techniques, respectively. The MWD curve data in FIGS. 30A and 30B demonstrated that the expected high M_w tail formation resulting from conventional diene branching occurred. The lack of significant movement of the peak MW with increasing diene branching is also apparent from the MWD curves.

[00221] The molecular weight distributional data in FIGS. 30A and 30B were reduced to simple metrics describing the evolution of the MWD curve position and shape as more diene monomers were fed to the CSTR. The data in Table 34 showed these MWD metrics for both absolute and conventional MWD measurements of the Guzman's polymer samples. Absolute MWD measurement data in Table 34 showed up to an 87% increase in molecular weight as 1,9-decadiene feed ranged from 0 to 923 ppm. Peak molecular weight change, as indicated by M_p, does not vary significantly for either means of molecular weight measurement, which is inconsistent with "Ladder branched" polymer results. The shape factors are summarized in Table 34 and are inconsistent with "Ladder branched" polymers because the values for both $G_{79/29}$ and A_{TAIL} increased as the diene feed level and M_w increased.

Table 34: Molecular weight data and metrics associated with examples in Table 33.

Ex.	Sample	Diene Feed (ppm)	Conventional GPC Metrics				Absolute GPC Metrics			
			M_w / M_{w0}	M_p / M_{p0}	$G_{(79/29)}$	A_{TAIL}	M_w / M_{w0}	M_p / M_{p0}	$G_{(79/29)}$	A_{TAIL}
33.C1	19	0	1.00	1.00	0.12	0.011	1.00	1.00	0.06	0.026
33.C2	20	523	1.24	1.02	0.22	0.043	1.22	0.99	0.18	0.062
33.C3	21	704	1.31	1.05	0.23	0.047	1.39	1.00	0.15	0.058
33.C4	22	794	1.40	1.02	0.27	0.051	1.53	1.00	0.13	0.062
33.C5	23	837	1.42	1.03	0.29	0.055	1.56	0.98	0.17	0.062
33.C6	24	881	1.53	1.09	0.26	0.061	1.69	1.07	0.20	0.066
33.C7	25	923	1.66	1.14	0.33	0.063	1.87	1.02	0.23	0.071

[00222] Some key parameters on commercial resins are tabulated in Table 35. Some of the basic parameters for materials were made in solution, gas phase, and high pressure reactors.

Table 35: Physical Characteristics of non-"Ladder Branched" Polymer Compositions

Example	Source Data	Resin	c-PDI	Average g'	$V_{0.1}$	V_{100}	Rheology Ratio (RR)	$Tan\delta_{0.1}$	$Tan\delta_{100}$
33.C1	DOWLEX 2045G	LLDPE	4.35	0.91	8,525	1,612	5.3	9.61	0.97
33.C2	ASPUNE 6835A	LLDPE	3.27	0.99	1,064	503	2.1	25.2	1.96
33.C3	ATTANE 4201	ULDPE	4.59	0.86	9,643	1,686	5.7	8.16	0.93
33.C4	ELITE™ 5800G	LDPE			966	304	3		
33.C5	Affinity™ PL 1880	LDPE			9,980	1,404	7.1		
33.C6	LDPE 722	LDPE	10.31	0.606	1987	254	7.8	6.01	1.01
33.C7	LDPE 5004I	LDPE	8.08	0.624	3420	335	10.2	4.73	0.922
33.C8	LDPE 662I	LDPE	11.55	0.548	21,078	646	32.6	1.63	0.70
33.C9	Exxon Resin 1*	LDPE	4.43	0.63	28,266	913	31.0	2.09	0.65
33.C10	Equistar Resin*	LDPE	7.67	0.54	37,944	730	52.0	1.26	0.59
33.C11	Exxon Resin 2*	LDPE	4.69	0.57	16,153	751	21.5	2.86	0.73
33.C8	US 9580533 (Slurry)	Ethylene-diene	14.15	0.979	9283	384.4	24.1	--	--
33.C12	US 9580533 (Solution)	Ethylene-diene	7.45	0.513	20162	521.5	38.7	--	--
33.C13	US 9580533 (Solution)	Ethylene-diene	3.68	0.880	173.8	134.2	1.3	--	--
33.C14	US 9580533 (Solution)	Ethylene-diene	5.28	0.718	16847.5	842.8	20.0	--	--
33.C15	US 9580533 (Solution)	Ethylene-diene	7.97	0.696	9893.2	569.6	17.4	--	--
33.C16	US 9580533 (Solution)	Ethylene-diene	5.71	0.593	1214.2	352.6	3.4	--	--

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*Competitor resins were tested as comparisons. The Exxon Resins were obtained from ExxonMobil. Equistar Resin is a LyondellBasell Petrothene product.

[00223] The data summarized in Table 35 are plotted in the graphs of FIG. 31 and FIG. 32. The data illustrates the difference in the "Ladder Branched" polymers in comparison to LDPE, LLDPE, ULDPE, and ethylene resins containing diene monomers. In FIG. 31 and FIG. 32, the "Ladder Branched" polymers (Ladder-PE in the legend of the graph) of this disclosure are clustered together, thus indicating that the "Ladder Branched" polymers have unique polymeric properties in comparison to other ethylene-based resins. As shown in the graph of FIG. 31, the "Ladder Branched" polymers have a rheology ratio at least 10, and an average g' less than 0.86. In FIG. 31, the LDPE resins plotted have an average g' of less than 0.65; the prior art ethylene-diene resins (listed as Prior Art ET-Diene in the legend) do not cluster together.

[00224] In FIG. 33, the melt strength (centiNewtons, cN) was measured as a function of the melt index (Log I_2). The polymers produced from the dual chain catalyst, as indicated by the triangles and the circles, were compared to a polymer produced from a single chain catalyst, and literature based curves of autoclave LDPE, tubular LDPE, and linear polyethylene. The melt strengths of the polymers produced from the dual chain catalysts were less than the melt strength of the autoclave LDPE, tubular LDPE, and the polymer produced from the single chain catalysts, but significantly greater than the linear polyethylene. This would indicate that the polymers produced from the dual chain catalysts have entangled, long-chain branching.

[00225] It should be apparent to those skilled in the art that various modifications can be made to the described embodiments without departing from the spirit and scope of the claimed subject matter. Thus, it is intended that the specification cover modifications and variations of the described embodiments provided such modification and variations come within the scope of the appended claims and their equivalents.

CLAIMS

1. A process of synthesizing long-chain branched copolymers, the process comprising:

contacting together one or more C_2-C_{14} alkene monomers, at least one diene or polyene, optionally a solvent, and a multi-chain catalyst, wherein the multi-chain catalyst comprises a plurality of polymerization sites;

producing at least two polymer chains of the C_2-C_{14} alkene monomers, each polymer chain polymerizing at one of the polymerization sites; and

synthesizing the long-chain branched polymers by connecting the two polymer chains with the diene or polyene, the joining of the two polymer chains being performed in a concerted manner during the polymerization.

2. The process of claim 1, wherein ethylene is added to such an extent that the resulting copolymer content is greater than 50 mol% ethylene.

3. The process of claims 1 or 2, wherein the diene and polyene comonomer is incorporated at such level to achieve at least one bridging juncture per 100 copolymer chains.

4. The process of any one of claims 1-3, wherein the diene is unconjugated or the polyene has at least two unconjugated bonds per molecule.

5. The process of any one of the preceding claims, wherein the multi-chain catalyst is a heterogeneous catalyst with surface concentration of metal atoms greater than or equal to 0.3 metal atoms per nanometer squared (metal/nm^2).

6. The process of any one of the preceding claims, wherein the multi-chain catalyst has two ligated transition metals linked by a dianionic activator where the distance between the metal atoms is less than or equal to 18.5 Å.

7. The process of any one of the preceding claims, wherein the multi-chain catalyst consists of two or more transition metals covalently tethered, where the distance between the metal atoms is less than or equal to 18.5 Å.

8. The process of any one of the preceding claims, wherein the multi-chain catalyst has two or more polymer chains on the same metal.

9. The process of any one of the preceding claims, wherein the multi-chain catalyst has a monoanionic ligand, is a Group IV Metal (Ti, Zr, Hf), and has two polymer chains on the same metal.

10. The process of any one of the preceding claims, wherein the long-chain branched copolymer M_w is at least 20% greater than the M_w of the polymer synthesized without the diene or polyene or wherein the long-chain branched copolymer M_p is at least 20% greater than the M_p of the polymer synthesized without the diene or polyene.

11. The process of any one of the preceding claims, wherein the polydisperse long-chain branched polymer has from 0.01 to 0.5 diene junctures per number average copolymer chain or 0.02 to 1.0 diene junctures per weight average copolymer chain.

12. The process of any one of the proceeding claims, wherein the polymerization occurs in a solution polymerization reactor or a particle forming polymerization reactor such as a slurry reactor or a gas phase reactor, wherein the molecular or solid-supported catalyst is delivered to the reaction media or developed in the reaction media, wherein the reactor system is batch or continuous or a hybrid such as semi-batch, wherein the reactor residence time distribution is narrow such as in non-backmixed reactors or broad such as in backmixed reactor and series and recycle reactors.