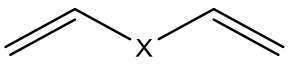
thereby causing gelling and reactor fouling. The reincorporation mechanism does not produce much branching, and branching can only occur after the polymer strand is produced, thereby further limiting the amount of branching that can occur.

SUMMARY

[0006] ~~Embodiments of t~~This disclosure include processes for synthesizing long-chain branched polymers. In one or more ~~embodiments~~examples, the process includes contacting together one or more C_2−C_{14} alkene monomers, at least one diene, optionally a solvent, and a multi-chain catalyst optionally in the presence of hydrogen, wherein the multi-chain catalyst comprises a plurality of polymerization sites. At least two polymer chains of the C_2−C_{14} alkene monomers are produced, each polymer chain polymerizing at one of the polymerization sites. Then, the long-chain branched polymers are synthesized by connecting the two polymer chains with the diene. The connecting of the two polymer chains being performed in a concerted manner during the polymerization. The tri-functional long chain branches are produced from the diene, wherein the long-chain branched polymers have a ratio of tri-functional to tetra-functional long chain branches from 0.05:1 to 100:0. The ratio of tri-functional to tetra-functional long chain branches may be adjusted by altering the feed ratio of C_2−C_{14} alkene monomer to hydrogen, if the ratio deviates from a target ratio of tri-functional to tetra-functional long chain branches.

[0007] In one or more ~~embodiments~~examples, the diene has a structure according to formula (I):



(I)

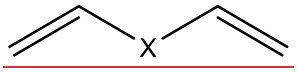
[0008] In formula (I), X is CR_2, SiR_2 or GeR_2, wherein each R is independently C_1−C_{12} hydrocarbyl or –H. In some ~~embodiments~~examples, X in formula (I) is $-C(R)_2-$, and wherein each R is –H or each R is C_1−C_{12} alkyl. In other ~~embodiments~~examples, X in formula (I) is $-Si(R)_2-$, and wherein each R is C_1−C_{12} alkyl. In one or more ~~embodiments~~examples, the diene is dimethyldivinylsilane.

[0009] Various ~~embodiments~~ examples 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.

[0009a] In one aspect, the present disclosure refers to a process of synthesizing long-chain branched polymers, the process comprising:

contacting together one or more C_2–C_{14} alkene monomers, at least one diene, optionally a solvent, and a multi-chain catalyst optionally in the presence of hydrogen, wherein the multi-chain catalyst is not a bimetallic catalyst and comprises heterogeneous catalyst or ligated transition metal catalyst having a plurality of polymerization sites, and wherein the diene has a structure according to formula (I):



where X is $-C(R)_2-$, $-Si(R)_2-$, or $-Ge(R)_2-$, wherein each R is independently C_1–C_{12} hydrocarbyl or –H;

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, the connecting of the two polymer chains being performed in a concerted manner during the polymerization, wherein the long-chain branched polymers have a ratio of tri-functional to tetra-functional long chain branches from 0.05:1 to 100:0; and

adjusting the ratio of tri-functional to tetra-functional long chain branches by altering the feed ratio of the C_2–C_{14} alkene monomers to hydrogen, if the ratio deviates from a target ratio of tri-functional to tetra-functional long chain branches.

BRIEF DESCRIPTION OF FIGURES

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

[0011] FIG. 2A is a plot of molecular weight increase versus diene linkages.

[0012] FIG. 2B is a plot of polydispersity vs. dienes linkages.

[0013] FIG. 3 is a graphical depiction of a predicted dependence of the molecular weight distribution (MWD) curve on tri-functional dienes branching level.

[0014] FIG. 4 is a graphical depiction of a predicted dependence of relative peak of the molecular weight (MW) on tri-functional dienes branching level.

[0015] FIG. 5 is a graphical depiction of the MWD curve illustrating how the high MWD tail area metrics are defined using the point of maximum slope.

[0016] FIG. 6. Conventional (RI) GPC of dimethyldivinylsilane samples with increasing amount of diene (Examples 1.C and 1.1-1.7).

[0017] FIG. 7 is an overall carbon NMR spectrum of dimethyldivinylsilane branched polyethylene (example 12.1).

[0018] FIG. 8 is the $Si(Me)_2$ region of the carbon NMR spectrum of dimethyldivinylsilane branched polyethylene (Example 12.1). Tri-functional LCB carbons = 0.17 Me /1000C and tetra-functional LCB carbons = 0.12 Me/1000C.

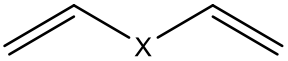
[0019] FIG. 9. Methine region of the carbon NMR spectrum of dimethyldivinylsilane branched polyethylene (Example 12.1). Tri-functional LCB = 0.09 CH /1000C, tetra-functional LCB = 0.16 CH/1000C.

[0020] FIG. 10. Conventional (RI) and absolute (LS) GPC for linear PE (Example 12.C) and dimethyldivinylsilane branched PE (Example 12.1).

CLAIMS

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

contacting together one or more C_2–C_{14} alkene monomers, at least one diene, optionally a solvent, and a multi-chain catalyst optionally in the presence of hydrogen, wherein the multi-chain catalyst is not a bimetallic catalyst and comprises heterogeneous catalyst or a ligated transition metal catalyst having a plurality of polymerization sites, and wherein the diene has a structure according to formula (I):



where X is $-C(R)_2-$, $-Si(R)_2-$, or $-Ge(R)_2-$, wherein each R is independently C_1–C_{12} hydrocarbyl or –H;

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, the connecting of the two polymer chains being performed in a concerted manner during the polymerization, wherein the long-chain branched polymers have a ratio of tri-functional to tetra-functional long chain branches from 0.05:1 to 100:0; and

adjusting the ratio of tri-functional to tetra-functional long chain branches by altering the feed ratio of the C_2–C_{14} alkene monomers to hydrogen, if the ratio deviates from a target ratio of tri-functional to tetra-functional long chain branches.

2. The process of claim 1, wherein X in formula (I) is $-C(R)_2-$, and wherein each R is –H.

3. The process of claim 1, wherein X in formula (I) is $-C(R)_2-$, and wherein each R is C_1–C_{12} alkyl.

4. The process of claim 1, wherein X in formula (I) is $-Si(R)_2-$, and wherein each R is C_1–C_{12} alkyl.

5. The process of claim 4, wherein the diene is dimethyldivinylsilane.

6. The process of any preceding claim, wherein the long-chain branched polymer is an ethylene-based copolymer comprising at least 50 mol% ethylene.

7. The process of any preceding claim, wherein the multi-chain catalyst is a heterogeneous catalyst with surface concentration of metal atoms greater than or equal to 1.5 metal atoms per nanometer squared (metal/nm^2).

8. The process of any preceding claim, wherein the multi-chain catalyst comprises a monoanionic ligand and a IUPAC Group IV metal selected from the group consisting of titanium, hafnium, or zirconium.

9. The process of any preceding claim, wherein the tri-functional long chain branches occur at a frequency of at least 0.05 per 1000 carbon atoms.

10. The process of any preceding claim, wherein the tri-functional long chain branches occur at a frequency of at least 0.1 per 1000 carbon atoms.

11. The process of any preceding claim, wherein the tri-functional long chain branches occur at a frequency of at least 0.2 per 1000 carbon atoms.

12. The process of any preceding claim, wherein the ratio of tri-functional to tetra-functional long chain branches is greater than 0.1:1.

13. The process of any preceding claim, wherein the controlling the ratio of tri-functional and tetra-functional long chain branches comprises increasing H_2 to increase the amount of tri-functional long chain branching.

14. The process claims 1 to 13, wherein the controlling the ratio of tri-functional and tetra-functional long chain branches comprises adjusting the ethylene to H_2 mole ratio to greater than 999:1 to yield less than 0.001:1 tri-functional to tetra-functional long chain branches.

15. The process of claims 1 to 13, wherein the controlling the ratio of tri-functional and tetra-functional long chain branches comprises adjusting the ethylene to H_2 mole ratio to less than 25:1 to yield greater than 0.5:1 tri-functional to tetra-functional long chain branches.

16. The process of claims 1 to 13, wherein the controlling the ratio of tri-functional and tetra-functional long chain branches comprises adjusting the ethylene to H_2 mole ratio to

less than 50:50 to yield greater than 1:1 tri-functional to tetra-functional long chain branches.

17. The process of any preceding claim, wherein the long-chain branched polymer has a weight average molecular weight (M_w) of less than 150,000 Daltons, as determined by gel permeation chromatography using a triple detector.

18. The process of any one of the proceeding claims, wherein the polymerization occurs in a solution polymerization reactor, a slurry reactor, a gas phase reactor, a batch reactor, a continuous reactor, a hybrid reactor, a non-backmixed reactors, a backmixed reactor, a series reactor, or a recycle reactor.

19. The process of any one of the proceeding claims, wherein the long-chain branched polymer have a molecular weight distribution (MWD) defined by the weight average molecular weight divided by the number average molecular weight (M_w/M_n) of less than 4 as determined by gel permeation chromatography using a triple detector.