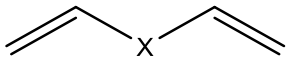
CLAIMS

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 a 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):


(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; and

producing tri-functional long chain branches from the diene, wherein the tri-functional long chain branches occur at a frequency of at least 0.03 per 1000 carbon atoms.

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 to 100:0.

13. 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.

14. 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.

15. 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.