What is claimed is:

1. A solution polymerization process for producing a high-cis polydiene, comprising:

polymerizing at least one conjugated diene monomer in an organic solvent in the presence of at least one thiol compound and a lanthanide-based catalyst composition to produce a polydiene having a cis-1,4-linkage of 90-99%,

wherein the at least one thiol compound is represented by the general formula R-S-H, where R is a hydrocarbyl group or a substituted hydrocarbyl group;

wherein the lanthanide-based catalyst composition comprises (a) a lanthanide compound, (b) an alkylating agent, and (c) a halogen source, where (c) may optionally be provided by (a), (b), or both (a) and (b);

wherein the molar ratio of the at least one thiol compound to the lanthanide compound ranges from 0.01:1 to 100:1; and

wherein either the at least one thiol compound is added to a mixture of the at least one conjugated diene monomer and the organic solvent prior to charging the mixture with the lanthanide-based catalyst composition or the lanthanide-based catalyst composition is added at the same time or shortly after the thiol compound is added to the organic solvent.

2. The process according to claim 1, wherein the molar ratio of the at least one thiol compound to the lanthanide compound ranges from 0.2:1 to 12:1.

3. The process according to claim 1, wherein the at least one thiol compound is selected from the group consisting of ethanethiol, propanethiols, butanethiols, pentanethiols, hexanethiols, heptanethiols, octanethiols, nonanethiols, decanethiols, dodecanethiols, tridecanethiols, tetradecanethiols, pentadecanethiols, hexadecanethiols, heptadecanethiols, octadecanethiols, nonadecanthiols, eicosanethiols, triacontanethiols, benzenethiol, alkyl-substituted benzenethiols, and combinations thereof.

4. The process of any one of claims 1-3,

wherein the lanthanide compound is selected from the group consisting of lanthanide carboxylates, lanthanide organophosphates, lanthanide organophosphonates, lanthanide organophosphinates, lanthanide carbamates, lanthanide dithiocarbamates, lanthanide xanthates, lanthanide β-diketonates, lanthanide alkoxides or aryloxides, lanthanide halides, lanthanide pseudo-halides, lanthanide oxyhalides, organolanthanide compounds, and combinations thereof, and the lanthanide portion of the lanthanide compound is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, didymium, and combinations thereof;

wherein the alkylating agent includes at least one organoaluminum compound, at least one organomagnesium compound, or combinations thereof; and

wherein the halogen source includes an elemental halogen, a mixed halogen, a hydrogen halide, an organic halide, an inorganic halide, a metallic halide, an organometallic halide, or combinations thereof.

5. The process of claim 4, wherein the at least one organoaluminum compound is selected from the group consisting of an aluminoxane, a compound represented by the general formula AlR_nX_{3-n}, and combinations thereof, where:

R is a monovalent organic group attached to the aluminum atom via a carbon atom,

X is a hydrogen atom, a halogen atom, a carboxylate group, an alkoxide group, or an aryloxide group, and

n is from 1 to 3.

6. The process of any one of claims 1-3, wherein the alkylating agent includes at least one aluminoxane and at least one organoaluminum compound other than aluminoxane.

7. The process of any one of claims 1-3, wherein the at least one conjugated diene monomer is a monomer selected from the group consisting of 1,3-butadiene, isoprene,

1,3-pentadiene, 1,3-hexadiene, 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2,4-hexadiene, and combinations thereof.

8. The process of any one of claims 1-3, wherein the polymerization takes place at 50° C to 120° C.

9. The process of any one of claims 1-3, wherein the polydiene has a polydispersity value of 1.5 to 3.5.

10. The process of any one of claims 1-3, wherein the polydiene has between 94% and 99% cis-1,4-linkage content.

11. An improved solution polymerization process for producing a high-cis polydiene by polymerizing at least one conjugated diene monomer in an organic solvent charged with a lanthanide-based catalyst composition, wherein the improvement comprises:

polymerizing the at least one conjugated diene monomer in the presence of at least one thiol compound in the organic solvent charged with the lanthanide-based catalyst composition to produce a polydiene having a cis-1,4-linkage content of 90-99%,

wherein the at least one thiol compound is represented by the general formula R-S-H, where R is a hydrocarbyl group or a substituted hydrocarbyl group;

wherein the polydiene produced has a higher cis-1,4-linkage content compared to a polydiene produced under the same polymerization conditions but without the at least one thiol compound;

wherein the molar ratio of the at least one thiol compound to the lanthanide compound ranges from 0.01:1 to 100:1; and

wherein either the at least one thiol compound is added to a mixture of the at least one conjugated diene monomer and the organic solvent prior to charging the mixture with the lanthanide-based catalyst composition or the lanthanide-based catalyst

composition is added at the same time or shortly after the thiol compound is added to the organic solvent.

12. The process of any one of claims 1 or 11, wherein the at least one thiol compound is a tertiary thiol.

13. The process of any one of claims 1 or 11, wherein the polydiene is polybutadiene.