CLAIMS

What is claimed is:

1. A process for the preparation of polybutene having an exo-olefin content of at least 50 mol. %, which process comprises contacting isobutene or an isobutene-containing monomer mixture, with a Lewis acid catalyst complexed with an oxygen and/or sulfur-containing Lewis base, in a substantially or completely apolar polymerization medium, and initiating polymerization of said isobutene or an isobutene-containing monomer mixture with an initiator, wherein said Lewis acid catalyst is a Lewis acid of the formula $MR"_mY_n$, wherein M is a metal selected from Al, Fe, Ga, Hf, Zr and W; R" is a hydrocarbyl group; Y is halogen; m is 0 or an integer of 1 to 5; and n is an integer of 1 to 6, with the proviso that m+n is equal to the valency of metal M; and the initiator is a compound of the formula RX, wherein X is a halide; R is a hydrocarbyl group capable of forming a stable carbocation and wherein the carbon linking group R to group X is tertiary, benzylic or allylic; and wherein said Lewis acid and said Lewis base are complexed in a solvent selected from liquid, apolar, non-halogenated aliphatic solvents, and liquid aromatic solvents.

2. The process of claim 1, wherein M is Al, Ga or Fe, and R" is a C_1 to C_8 alkyl group.

3. The process of claim 1, wherein M is Al or Fe.

4. The process of claim 1, wherein Y is Cl or Br.

5. The process of claim 1, wherein said Lewis base is selected from acyclic dihydrocarbyl ethers, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, basic cyclic ethers having a 5 to 7 membered cyclic group, dihydrocarbyl ketones, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, C_1 to C_{12} aliphatic alcohols, C_1 to C_{12} aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, and basic dihydrocarbyl thiocarbonyl compounds,

wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, and mixtures thereof.

6. The process of claim 5, wherein said Lewis base is selected from acyclic dialkyl ethers, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, cyclic ethers having a 5 to 7 membered cyclic group, basic dialkyl ketones, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, C_1 to C_4 aliphatic alcohols, C_1 to C_4 aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C_1 to C_4 alkyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, and dialkyl thiocarbonyl compounds, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, and mixtures thereof.

7. The process of claim 5, wherein said Lewis base is a dihydrocarbyl ether or dihydrocarbyl ketone, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ether Lewis base is substituted with an electron-withdrawing group.

8. The process of claim 7, wherein said electron-withdrawing group is a halogen atom.

9. The process of claim 8, wherein said halogen atom is chlorine.

10. The process of claim 5, wherein said hydrocarbyl groups of said Lewis bases are branched or straight-chained C_1 to C_4 alkyl groups.

11. The process of claim 7, wherein said hydrocarbyl groups of said Lewis bases are branched or straight-chained C_1 to C_4 alkyl groups.

12. The process of claim 1, wherein said solvent is a liquid, apolar, non-halogenated aliphatic solvent, and $m \geq 1$.

13. The process of claim 1, wherein said solvent is a liquid, aromatic solvent selected from benzene, chlorobenzene, toluene and xylene.

14. The process of claim 13, wherein said solvent is toluene or xylene.

15. The process of claim 1, wherein said apolar polymerization medium is selected from saturated C_4 hydrocarbons, unsaturated C_4 hydrocarbons, and mixtures thereof.

16. The process of claim 1, wherein said isobutene or an isobutene-containing monomer mixture is selected from pure isobutene; a C_4 refinery cut containing between about 5% and about 50% butene-1, between about 2% and about 40% butene-2, between about 2% and about 60% iso-butane, between about 2% and about 20% n-butane, and up to about 0.5% butadiene, wherein all percentages are by mass, based on the total mass of the C_4 refinery cut; and mixtures of pure isobutene and said C_4 refinery cut.

17. The process of claim 1, wherein said complex is contacted with said isobutene or an isobutene-containing monomer at a concentration of millimoles of Lewis acid-Lewis base complex per liter of medium of from about 0.2 mM to about 200 mM.

18. The process of claim 1, wherein said Lewis acid and said Lewis base are complexed by dissolving the Lewis acid in said solvent to form a solution, and then adding said Lewis base to said solution.

19. The process of claim 14, wherein said solvent is selected from xylene and toluene, and said Lewis Acid and said Lewis base are complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution.

20. The process of claim 1, wherein the polymerization process is conducted continuously.

21. The process of claim 1, wherein said polybutene product has an exo-olefin content of at least 70 mol. %.

22. A catalyst-initiator system for catalyzing the polymerization of isobutene or an isobutene-containing monomer mixture in a substantially or completely apolar polymerization medium to provide a polybutene product having an exo-olefin content of at least 50 mol. %, wherein said catalyst comprising a Lewis acid catalyst

complexed with an oxygen and/or sulfur containing Lewis base, wherein said Lewis acid catalyst is a Lewis acid of the formula $MR"_mY_n$, wherein M is a metal selected from Al, Fe, Ga, Hf, Zr and W; R" is a hydrocarbyl group; Y is halogen; m is 0 or an integer of 1 to 5; and n is an integer of 1 to 6, with the proviso that m+n is equal to the valency of metal M; and the polymerization is initiated via an initiator of the formula RX, wherein X is a halide; R is a hydrocarbyl group capable of forming a stable carbocation, and wherein the carbon linking group R to group X is tertiary, benzylic or allylic; and wherein said Lewis acid and said Lewis base are complexed in a solvent selected from liquid, apolar, non-halogenated aliphatic solvents, and liquid aromatic solvents.

23. The catalyst-initiator system of claim 22, wherein M is Al, Ga or Fe, and R" is a C_1 to C_8 alkyl group.

24. The catalyst-initiator system of claim 23, wherein M is Al or Fe.

25. The catalyst-initiator system of claim 22, wherein Y is Cl or Br.

26. The catalyst-initiator system of claim 22, wherein said Lewis base is selected from acyclic dihydrocarbyl ethers, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, basic cyclic ethers having a 5 to 7 membered cyclic group, dihydrocarbyl ketones, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, C_1 to C_{12} aliphatic alcohols, C_1 to C_{12} aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, and basic dihydrocarbyl thiocarbonyl compounds, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, and mixtures thereof

27. The catalyst-initiator system of claim 26, wherein said Lewis base is selected from acyclic dialkyl ethers, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, cyclic ethers having a 5 to 7 membered cyclic group, basic dialkyl ketones, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, C_1 to C_4

aliphatic alcohols, C_1 to C_4 aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C_1 to C_4 alkyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, and dialkyl thiocarbonyl compounds, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, and mixtures thereof.

28. The catalyst-initiator system of claim 26, wherein said Lewis base is a dihydrocarbyl ether or a dihydrocarbyl ketone, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ether Lewis base is substituted with an electron-withdrawing group.

29. The catalyst-initiator system of claim 28, wherein said electron-withdrawing group is a halogen atom.

30. The catalyst-initiator system of claim 29, wherein said halogen atom is chlorine.

31. The catalyst-initiator system of claim 28, wherein said hydrocarbyl groups of said Lewis bases are branched or straight-chained C_1 to C_4 alkyl groups.

32. The catalyst-initiator system of claim 30, wherein said hydrocarbyl groups of said Lewis bases are branched or straight-chained C_1 to C_4 alkyl groups.

33. The catalyst-initiator system of claim 22, wherein said solvent is a liquid, apolar, non-halogenated aliphatic solvent, and $m \geq 1$.

34. The catalyst-initiator system of claim 22, wherein said solvent is a liquid, aromatic solvent selected from benzene, chlorobenzene, toluene and xylene.

35. The catalyst-initiator system of claim 34, wherein said solvent is toluene or xylene.

36. The catalyst-initiator system of claim 22, wherein said Lewis acid and said Lewis base are complexed by dissolving the Lewis acid in solvent to form a solution, and then adding said Lewis base to said solution.

37. The catalyst-initiator system of claim 22, wherein said solvent is selected from benzene and toluene and said Lewis acid and said Lewis base are complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution.

38. The process of claim 1, wherein said Lewis acid is selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ and n-$BuAlCl_2$; said Lewis base is a dihydrocarbyl ether, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, and wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ether Lewis base is substituted with chlorine; said solvent is selected from benzene and toluene and said Lewis acid and said Lewis base are complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in the complex is from about 1:1 to about 1:1.7.

39. The catalyst-initiator system of claim 22, wherein said Lewis acid is selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ and n-$BuAlCl_2$; said Lewis base is a dihydrocarbyl ether, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, and wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ether Lewis base is substituted with chlorine; said solvent is selected from benzene and toluene and said Lewis acid and said Lewis base are complexed by dissolving said Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in said complex is from about 1:1 to about 1:1.7.

40. The process of claim 1, wherein said Lewis acid is selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ and n-$BuAlCl_2$; said Lewis base is a dihydrocarbyl ketone, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, and wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ketone is substituted with chlorine; said solvent is selected from benzene and toluene and said Lewis acid

and said Lewis base are complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in the complex is from about 1:1 to about 1:1.7.

41. The catalyst-initiator system of claim 22, wherein said Lewis acid is selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ and n-$BuAlCl_2$; said Lewis base is a dihydrocarbyl ketone, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, and wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ketone is substituted with chlorine; said solvent is selected from benzene and toluene and said Lewis acid and said Lewis base are complexed by dissolving said Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in said complex is from about 1:1 to about 1:1.7.

CLAIMS

What is claimed is:

1. A process for the preparation of polybutene having an exo-olefin content of at least 50 mol %, which process comprises complexing a Lewis acid catalyst with an oxygen and/or sulfur-containing Lewis base in a solvent selected from liquid, apolar, non-halogenated aliphatic solvents, or and liquid aromatic solvents, contacting isobutene or an isobutene-containing monomer mixture, with the resulting Lewis acid/Lewis base complex, in a substantially or completely apolar polymerization medium, and initiating polymerization of said isobutene or an isobutene-containing monomer mixture with an initiator, wherein said Lewis acid catalyst is a Lewis acid of the formula $MR"_mY_{n,}$ wherein M is a metal selected from Al, Fe, Ga, Hf, Zr W; R" is a hydrocarbyl group; Y is halogen; m is 0 or an integer of 1 to 5, n is an integer of 1 to 6 and m+n is equal to the valency of metal M, with the proviso that, when M is Al, m is 1 and when said solvent is a liquid, apolar, non-halogenated aliphatic solvent, m is at least 1; and the initiator is a compound of the formula RX, wherein X is a halide; R is a hydrocarbyl group that forms a stable carbocation, and wherein the carbon linking group R to group X is tertiary, benzylic or allylic.

2. The process of claim 1, wherein M is Al, Ga or Fe, and R" is a C_1 to C_8 alkyl group.

3. The process of claim 1, wherein M is Al or Fe.

4. The process of claim 1, wherein Y is Cl or Br.

5. The process of claim 1, wherein said Lewis base is selected from acyclic dihydrocarbyl ethers, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, cyclic ethers having a 5 to 7 membered cyclic group, dihydrocarbyl ketones, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, C_1 to C_{12} aliphatic alcohols, C_1 to C_{12} aliphatic aldehydes, acyclic aliphatic hydrocarbyl esters wherein the hydrocarbyl group is selected from C_1 to C_{12} hydrocarbyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each alkyl group is independently selected from C_1 to C_{12} alkyl,

dihydrocarbyl thiocarbonyl compounds, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, or mixtures thereof.

6. The process of claim 5, wherein said Lewis base is selected from acyclic dialkyl ethers, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, cyclic ethers having a 5 to 7 membered cyclic group, dialkyl ketones, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, C_1 to C_4 aliphatic alcohols, C_1 to C_4 aliphatic aldehydes, acyclic aliphatic hydrocarbyl esters wherein the hydrocarbyl group is selected from C_1 to C_4 alkyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, dialkyl thiocarbonyl compounds, wherein each alkyl group is independently selected from C_1 to C_4 alkyl, or mixtures thereof.

7. The process of claim 5, wherein said Lewis base is a dihydrocarbyl ether or dihydrocarbyl ketone, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ether or dihydrocarbyl ketone is substituted with an electron-withdrawing group.

8. The process of claim 7, wherein said electron-withdrawing group is a halogen atom.

9. The process of claim 8, wherein said halogen atom is chlorine.

10. The process of claim 5, wherein said hydrocarbyl groups of said Lewis bases are branched or straight-chained C_1 to C_4 alkyl groups.

11. The process of claim 7, wherein said hydrocarbyl groups of said Lewis bases are branched or straight-chained C_1 to C_4 alkyl groups.

12. The process of claim 1, wherein said solvent is a liquid, apolar, non-halogenated aliphatic solvent, and $m > 1$.

13. The process of claim 1, wherein said solvent is a liquid, aromatic solvent selected from benzene, chlorobenzene, toluene or xylene.

14. The process of claim 13, wherein said solvent is toluene or xylene.

15. The process of claim 1, wherein said apolar polymerization medium is selected from saturated C_4 hydrocarbons, unsaturated C_4 hydrocarbons, or mixtures thereof.

16. The process of claim 1, wherein said isobutene or an isobutene-containing monomer mixture is selected from pure isobutene; a C_4 refinery cut containing between about 5% and about 50% butene-1, between about 2% and about 40% butene-2, between about 2% and about 60% iso-butane, between about 2% and about 20% n-butane, and up to about 0.5% butadiene, wherein all percentages are by mass, based on the total mass of the C_4 refinery cut; or mixtures of pure isobutene and said C_4 refinery cut.

17. The process of claim 1, wherein said complex is contacted with said isobutene or an isobutene-containing monomer at a concentration of millimoles of Lewis acid-Lewis base complex per liter of medium of from about 0.2 mM to about 200 mM.

18. The process of claim 1, wherein said Lewis acid and said Lewis base are complexed by dissolving the Lewis acid in said solvent to form a solution, and then adding said Lewis base to said solution.

19. The process of claim 14, wherein said solvent is selected from xylene or toluene, and said Lewis Acid and said Lewis base are complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution.

20. The process of claim 1, wherein the polymerization process is conducted continuously.

21. The process of claim 1, wherein said polybutene product has an exo-olefin content of at least 70 mol %.

22. A catalyst-initiator system for catalyzing the polymerization of isobutene or an isobutene-containing monomer mixture in a substantially or completely apolar polymerization medium to provide a polybutene product having an exo-olefin content of at least 50 mol %, wherein said

catalyst consists essentially of a Lewis acid catalyst complexed with an oxygen and/or sulfur containing Lewis base in a solvent selected from liquid, apolar, non-halogenated aliphatic solvents, or liquid aromatic solvents, wherein said Lewis base is a dihydrocarbyl ketone, wherein each hydrocarbyl group of said dihydrocarbyl ketone is independently selected from C_1 to C_8 hydrocarbyl, and wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ketone is substituted with chlorine, and said Lewis acid catalyst is a Lewis acid of the formula $MR"_mY_{n,}$ wherein M is a metal selected from Al, Fe, Ga, Hf, Zr or W; R" is a hydrocarbyl group; Y is halogen; m is 0 or an integer of 1 to 5, n is an integer of 1 to 6, and m+n is equal to the valency of metal M with the proviso that, when M is Al, m is 1 and when said solvent is a liquid, apolar, non-halogenated aliphatic solvent, m is at least 1; and wherein said initiator is a compound of the formula RX, wherein X is a halide; R is a hydrocarbyl group that forms a stable carbocation, and wherein the carbon linking group R to group X is tertiary, benzylic or allylic.

23. The catalyst-initiator system of claim 22, wherein M is Al, Ga or Fe, and R" is a C_1 to C_8 alkyl group.

24. The catalyst-initiator system of claim 23, wherein M is Al or Fe.

25. The catalyst-initiator system of claim 22, wherein Y is Cl or Br.

26. The catalyst-initiator system of claim 22, wherein said solvent is a liquid, apolar, non-halogenated aliphatic solvent, and m > 1.

27. The catalyst-initiator system of claim 22, wherein said solvent is a liquid, aromatic solvent selected from benzene, chlorobenzene, toluene or xylene.

28. The catalyst-initiator system of claim 27, wherein said solvent is toluene or xylene.

29. The catalyst-initiator system of claim 22, wherein said Lewis acid and said Lewis base are complexed by dissolving the Lewis acid in solvent to form a solution, and then adding said Lewis base to said solution.

30. The catalyst-initiator system of claim 22, wherein said solvent is selected from benzene or toluene and said Lewis acid and said Lewis base are complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution.

31. The process of claim 1, wherein said Lewis acid is selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ or n-$BuAlCl_2$; said Lewis base is a dihydrocarbyl ether, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, and wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ether is substituted with chlorine; said solvent is selected from benzene or toluene and said Lewis acid and said Lewis base is complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in the complex is from about 1:1 to about 1:1.7.

32. The process of claim 1, wherein said Lewis acid is selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ or n-$BuAlCl_2$, and said solvent is selected from benzene and toluene and said Lewis acid and said Lewis base are complexed by dissolving the Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in the complex is from about 1:1 to about 1:1.7.

33. The catalyst-initiator system of claim 22, wherein said Lewis acid is selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ or n-$BuAlCl_2$; and said solvent is selected from benzene or toluene and said Lewis acid and said Lewis base are complexed by dissolving said Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in said complex is from about 1:1 to about 1:1.7.

34. A catalyst-initiator system for catalyzing the polymerization of isobutene or an isobutene-containing monomer mixture in a substantially or completely apolar polymerization medium to provide a polybutene product having an exo-olefin content of at least 50 mol %, wherein said catalyst consists essentially of a Lewis acid catalyst complexed with an oxygen and/or sulfur containing Lewis base in a solvent selected from benzene and toluene, wherein said Lewis acid catalyst is a Lewis acid selected from $MeAlCl_2$, $EtAlCl_2$, iso-$BuAlCl_2$ or n-$BuAlCl_2$, and wherein

said Lewis base is a dihydrocarbyl ketone, wherein each hydrocarbyl group is independently selected from C_1 to C_8 hydrocarbyl, and wherein one or each of said hydrocarbyl groups of said dihydrocarbyl ketone is substituted with chlorine, and said Lewis acid and said Lewis base are complexed by dissolving said Lewis base in said solvent to form a solution, and then adding said Lewis acid to said solution in an amount such that the molar ratio of Lewis acid to Lewis base in said complex is from about 1:1 to about 1:1.7.