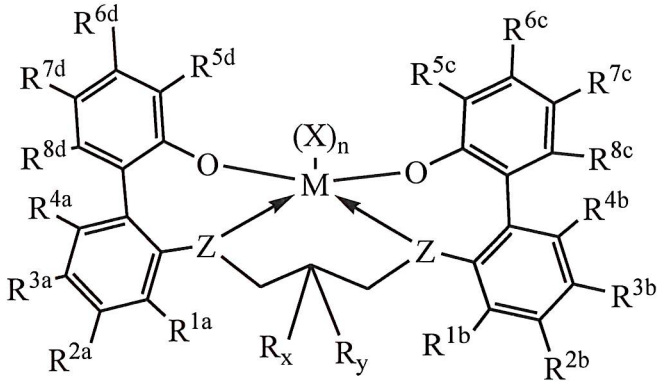
SUMMARY

The disclosure provides a process to form an ethylene-based polymer, said process comprising polymerizing ethylene, and optionally at least one comonomer, in the presence of at least one molecular transition metal complex selected from Formula 1:



(Formula 1),

wherein M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4;

n is an integer of from 0 to 3, wherein when n is 0, X is absent;

each X is independently a monodentate ligand that is neutral, monoanionic, or dianionic, or two X are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic;

X and n are selected such that the metal-ligand complex is neutral;

each Z moiety is, independently, -O-, -S-, -N[(C_1-C_{40})hydrocarbyl]-, or -P[(C_1-C_{40})hydrocarbyl]-;

R_x is selected from the following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl; a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl: -Si(R^C)$_3$, -OSi(R^C)$_3$ -Ge(R^C)$_3$, -P(R^C)$_2$, -N(R^C)$_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -OCF_3, -S(O)R^C, -S(O)$_2$$R^C$, -N=C($R^C$)$_2$, -OC(O)$R^C$, -C(O)O$R^C$, -N(R)C(O)$R^C$, -C(O)N($R^C$)$_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl;

R_y is selected from the following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl; a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl; -Si(R^C)$_3$, -OSi(R^C)$_3$, -Ge(R^C)$_3$, -P(R^C)$_2$, -N(R^C)$_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -OCF_3 , -S(O)R^C, -S(O)$_2$$R^C$, -N=C($R^C$)$_2$, -OC(O)$R^C$, -C(O)O$R^C$, -N(R)C(O)$R^C$, -C(O)N($R^C$)$_2$, a halogen, or a hydrogen;

and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, when Rx is hydrogen, Ry is not hydrogen, and when Ry is hydrogen, Rx is not hydrogen; and

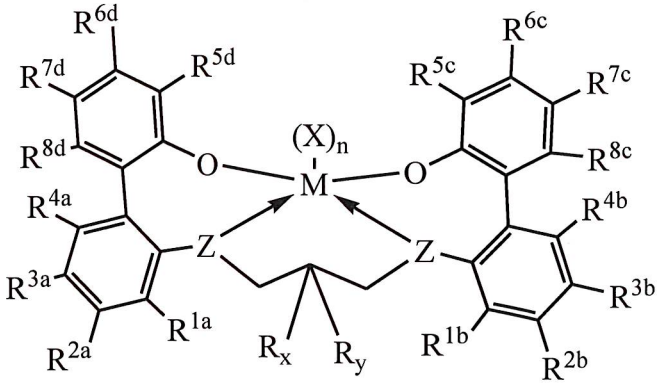
wherein Rx and Ry may optionally form a ring structure; and

wherein R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} are each, independently, selected from the following: a substituted or unsubstituted $(C_1\text{-}C_{40})$-hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, $-Si(R^C)_3$, $-OSi(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, for Formula 1, one or more hydrogen atoms may optionally be substituted with deuterium, and

wherein, for Formula 1, two or more of R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} may optionally form one or more ring structures.

In one aspect, there is provided a process to form an ethylene-based polymer, said process comprising polymerizing ethylene, and optionally at least one comonomer, in the presence of at least one molecular transition metal complex selected from Formula 1:



(Formula 1),

wherein M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4;

each X is independently a monodentate ligand that is neutral, monoanionic, or dianionic, or two X are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic;

X and n are selected such that the metal-ligand complex is neutral;

each Z moiety is, independently, -O-, -S-, -N[(C_1-C_{40})hydrocarbyl]-, or -P[(C_1-C_{40})hydrocarbyl]-;

R_x is selected from the following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl; a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl: -Si(R^C)$_3$, -OSi(R^C)$_3$ -Ge(R^C)$_3$, -P(R^C)$_2$, -N(R^C)$_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -OCF_3, -S(O)R^C, -S(O)$_2$$R^C$, -N=C($R^C$)$_2$, -OC(O)$R^C$, -C(O)O$R^C$, -N(R)C(O)$R^C$, -C(O)N($R^C$)$_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl;

R_y is selected from the following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl; a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl; -Si(R^C)$_3$, -OSi(R^C)$_3$, -Ge(R^C)$_3$, -P(R^C)$_2$, -N(R^C)$_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -OCF_3 , -S(O)R^C, -S(O)$_2$$R^C$, -N=C($R^C$)$_2$, -OC(O)$R^C$, -C(O)O$R^C$, -N(R)C(O)$R^C$, -C(O)N($R^C$)$_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

wherein, when Rx is hydrogen, Ry is not hydrogen, and when Ry is hydrogen, Rx is not hydrogen; and

wherein Rx and Ry may optionally form a ring structure; and

wherein R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} are each, independently, selected from the following: a substituted or unsubstituted (C_1-C_{40})-hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, -Si(R^C)$_3$, -OSi(R^C)$_3$, -Ge(R^C)$_3$, -P(R^C)$_2$, -N(R^C)$_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -OCF_3, -S(O)R^C, -S(O)$_2$$R^C$, -N=C($R^C$)$_2$, -OC(O)$R^C$, -C(O)O$R^C$, -N(R)C(O)$R^C$, -C(O)N($R^C$)$_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

wherein, for Formula 1, one or more hydrogen atoms may optionally be substituted with deuterium, and

wherein, for Formula 1, two or more of R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} may optionally form one or more ring structures; wherein n is 2, and each X is independently an alkyl; and wherein the ethylene-based polymer has a melt viscosity, at 177°C, less than, or equal to, 50,000 cP.

In another aspect, there is provided an ethylene-based polymer formed from the process disclosed herein.

In another aspect, there is provided a composition comprising the ethylene-based polymer disclosed herein.

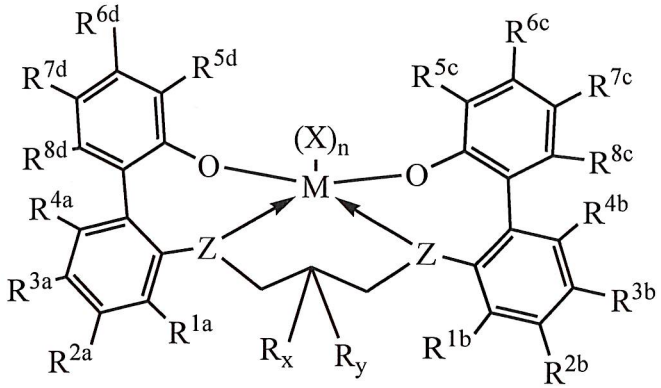
The disclosure also provides a transition metal complex of Formula 1.

DETAILED DESCRIPTION OF THE EMBODIMENTS

A group of novel bis-biphenyl-phenoxy based transition metal complexes have been discovered, which can operate at high polymerization temperatures (for example, ≥ 170°C) and low levels of hydrogen, for the production of low molecular weight ethylene-based polymers with melt viscosities ≤ 50,000 cP (at 177°C). Preferably, such polymers also have low densities (≤ 0.90 g/cc). By addition of a single alkyl group to the central carbon of a C3 bridged transition metal based bis-biphenyl-phenoxy catalyst, the molecular weight of the polymer product can be drastically decreased, without diminishing comonomer incorporation capability or high temperature performance. The inventive process surprisingly offers the advantage of greatly reducing molecular weight of a given ethylene-based polymer, without otherwise significantly modifying the nature of the homopolymerization or copolymerization. This molecular weight reduction, in turn, may offer a significant increase in flow behavior,

CLAIMS

1. A process to form an ethylene-based polymer, said process comprising polymerizing ethylene, and optionally at least one comonomer, in the presence of at least one molecular transition metal complex selected from Formula 1:



(Formula 1),

wherein M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4;

each X is independently a monodentate ligand that is neutral, monoanionic, or dianionic, or two X are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic;

X and n are selected such that the metal-ligand complex is neutral;

each Z moiety is, independently, -O-, -S-, -N[(C_1-C_{40})hydrocarbyl]-, or -P[(C_1-C_{40})hydrocarbyl]-;

R_x is selected from the following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl; a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl: -Si(R^C)$_3$, -OSi(R^C)$_3$ -Ge(R^C)$_3$, -P(R^C)$_2$, -N(R^C)$_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -OCF_3, -S(O)R^C, -S(O)$_2$$R^C$, -N=C($R^C$)$_2$, -OC(O)$R^C$, -C(O)O$R^C$, -N(R)C(O)$R^C$, -C(O)N($R^C$)$_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl;

R_y is selected from the following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl; a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl; -Si(R^C)$_3$, -OSi(R^C)$_3$, -Ge(R^C)$_3$, -P(R^C)$_2$, -N(R^C)$_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -OCF_3 , -S(O)R^C, -S(O)$_2$$R^C$, -N=C($R^C$)$_2$,

$-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, when Rx is hydrogen, Ry is not hydrogen, and when Ry is hydrogen, Rx is not hydrogen; and

wherein Rx and Ry may optionally form a ring structure; and

wherein R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} are each, independently, selected from the following: a substituted or unsubstituted $(C_1\text{-}C_{40})$-hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, $-Si(R^C)_3$, $-OSi(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, for Formula 1, one or more hydrogen atoms may optionally be substituted with deuterium, and

wherein, for Formula 1, two or more of R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} may optionally form one or more ring structures;

wherein n is 2, and each X is independently an alkyl; and wherein the ethylene-based polymer has a melt viscosity, at 177°C, less than, or equal to, 50,000 cP.

2. The process of claim 1 wherein at least one of R^{3a} or R^{3b} is a halogen.

3. The process of claim 1 or claim 2, wherein Rx or Ry is hydrogen, and the other is a substituted or unsubstituted (C1-C40) hydrocarbyl.

4. The process of claim 3, wherein Rx or Ry is hydrogen, and the other is an unsubstituted (C1-C20) hydrocarbyl.

5. The process of any one of the previous claims, wherein each Z is –O- (oxygen atom).

6. The process of any one of the previous claims, wherein R^{5c} and R^{5d} are each independently selected from the following: 1,2,3,4-tetrahydronaphthyl; anthracenyl; 1,2,3,4-tetrahydroanthracenyl; 1,2,3,4,5,6,7,8-octahydroanthracenyl; phenanthrenyl; 1,2,3,4,5,6,7,8-octahydrophenanthrenyl; 2,6-dimethylphenyl; 2,6-diisopropylphenyl; 3,5-di(tertiary-butyl)phenyl; 3,5-diphenylphenyl; 1-naphthyl; 2-methyl-1-naphthyl; 2-naphthyl; 1,2,3,4-tetra-hydronaphth-5-yl; 1,2,3,4-tetrahydronaphth-6-yl; anthracen-9-yl; 1,2,3,4-tetrahydro-anthracen-9-yl; 1,2,3,4,5,6,7,8-octahydroanthracen-9-yl; 1,2,3,4,5,6,7,8-octahydrophenanthren-9-yl; indolyl; indolinyl; quinolinyl; 1,2,3,4-tetrahydroquinolinyl; isoquinolinyl; 1,2,3,4-tetrahydro-isoquinolinyl; carbazolyl; 1,2,3,4-tetrahydrocarbazolyl; 1,2,3,4,5,6,7,8-octahydrocarbazolyl; 3,6-di(tertiary-butyl)-carbazol-9-yl; 3,6-di(tertiary-octyl)-carbazol-9-yl; 3,6-diphenylcarbazol-9-yl; 3,6-bis(2,4,6-trimethylphenyl)-carbazol-9-yl; 2,7-di(tertiary-butyl)-carbazol-9-yl; 2,7-di(tertiary-octyl)-carbazol-9-yl; 2,7-diphenylcarbazol-9-yl; or 2,7-bis(2,4,6-trimethylphenyl)-carbazol-9-yl.

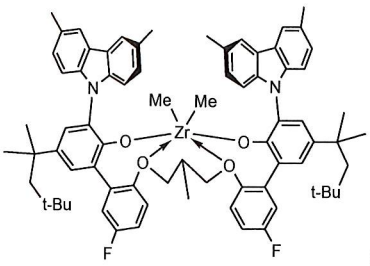
7. The process of any one of the previous claims, wherein R^{7c} and R^{7d} are each independently an alkyl.

8. The process of any one of the previous claims, wherein R^{1a}, R^{2a}, R^{4a}, R^{1b}, R^{2b}, R^{4b}, R^{6c}, R^{8c}, R^{6d} and R^{8d} are each hydrogen.

9. The process of any one of the previous claims, wherein the process is run at a polymerization temperature greater than, or equal to, 170°C.

10. The process of any one of the previous claims, wherein the ethylene-based polymer is an ethylene/α-olefin copolymer.

11. The process of any one of the previous claims, wherein Formula 1 is selected from the following structures a) through dd):



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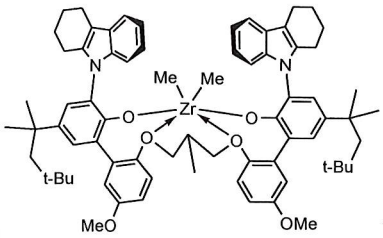

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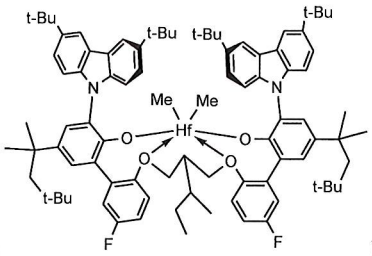

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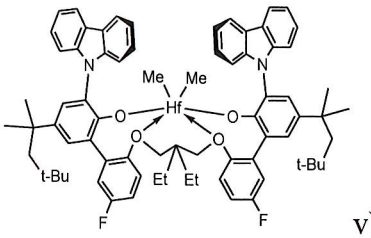

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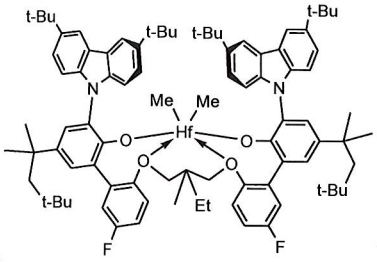

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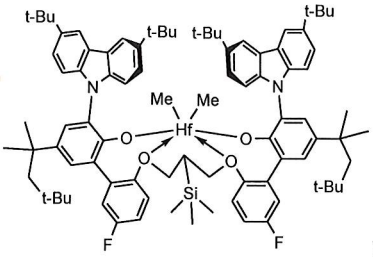

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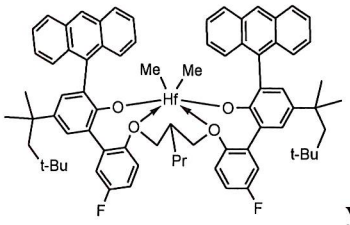

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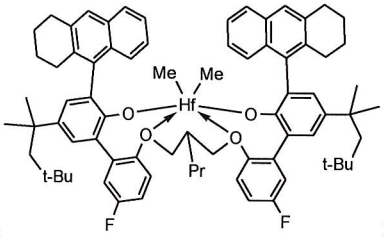

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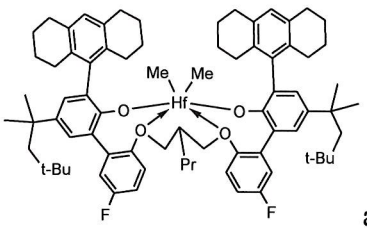

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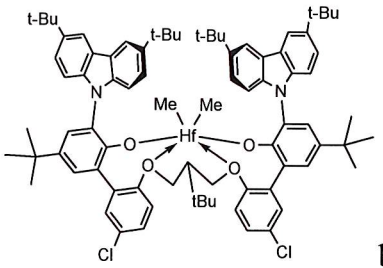

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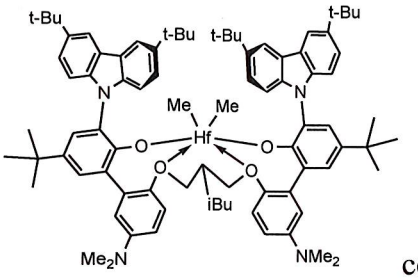

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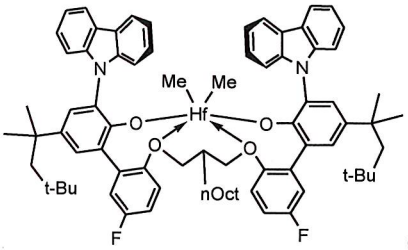

dd).

12. An ethylene-based polymer formed from the process of any one of the previous claims.

13. A composition comprising the ethylene-based polymer of claim 12.