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(72) Inventeurs/Inventors:
LAUGHNER, MICHAEL K., US;
MANGOLD, DEBRA J., US;
PARIKH, DEEPAK R., US

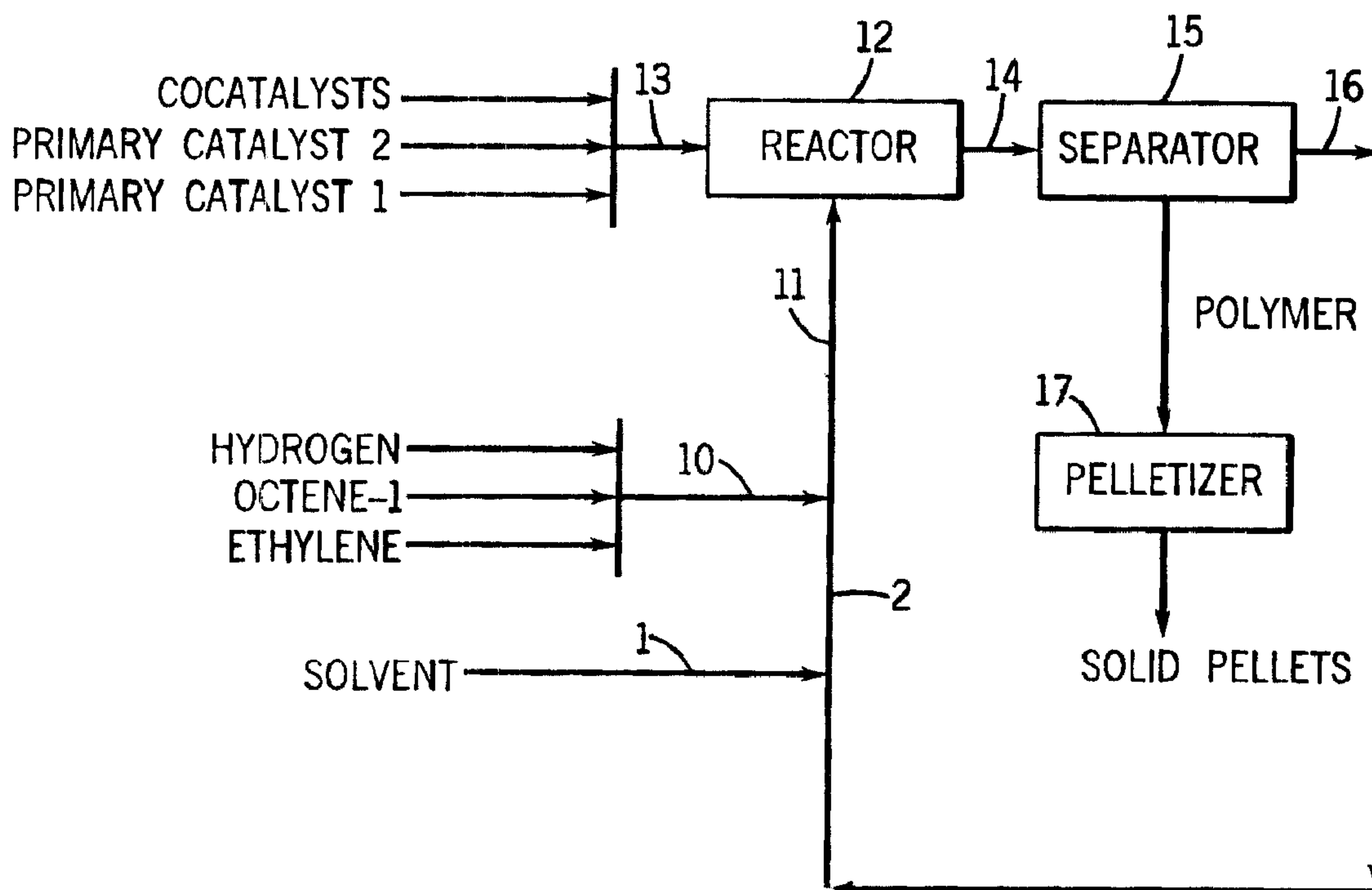
(73) Propriétaire/Owner:
DOW GLOBAL TECHNOLOGIES INC., US

(74) Agent: SMART & BIGGAR

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Ethylene-based polymer blends having an MWD of at least 2 were made in a single reactor using a mixed constrained geometry catalyst (CGC) system. The process comprises the steps of contacting under polymerization conditions and in a single reaction vessel (i) ethylene, (ii) at least one C₃-C₂₀ α -olefin, (iii) optionally, at least one polyene, and (iv) a mixed CGC system.

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Deepak, R. [US/US]; 59 North Trillium Court, Lake Jackson, TX 77566 (US).

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(74) Agents: **PLOTECHER, Gary, R.** et al.; Whyte Hirschboeck Dudek S.C., Suite 2100, 111 E. Wisconsin Avenue, Milwaukee, WI 53202 (US).

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(71) Applicant (*for all designated States except US*): **DUPONT DOW ELASTOMERS L.L.C.** [US/US]; 300 Bellevue Parkway, Wilmington, DE 19809 (US).

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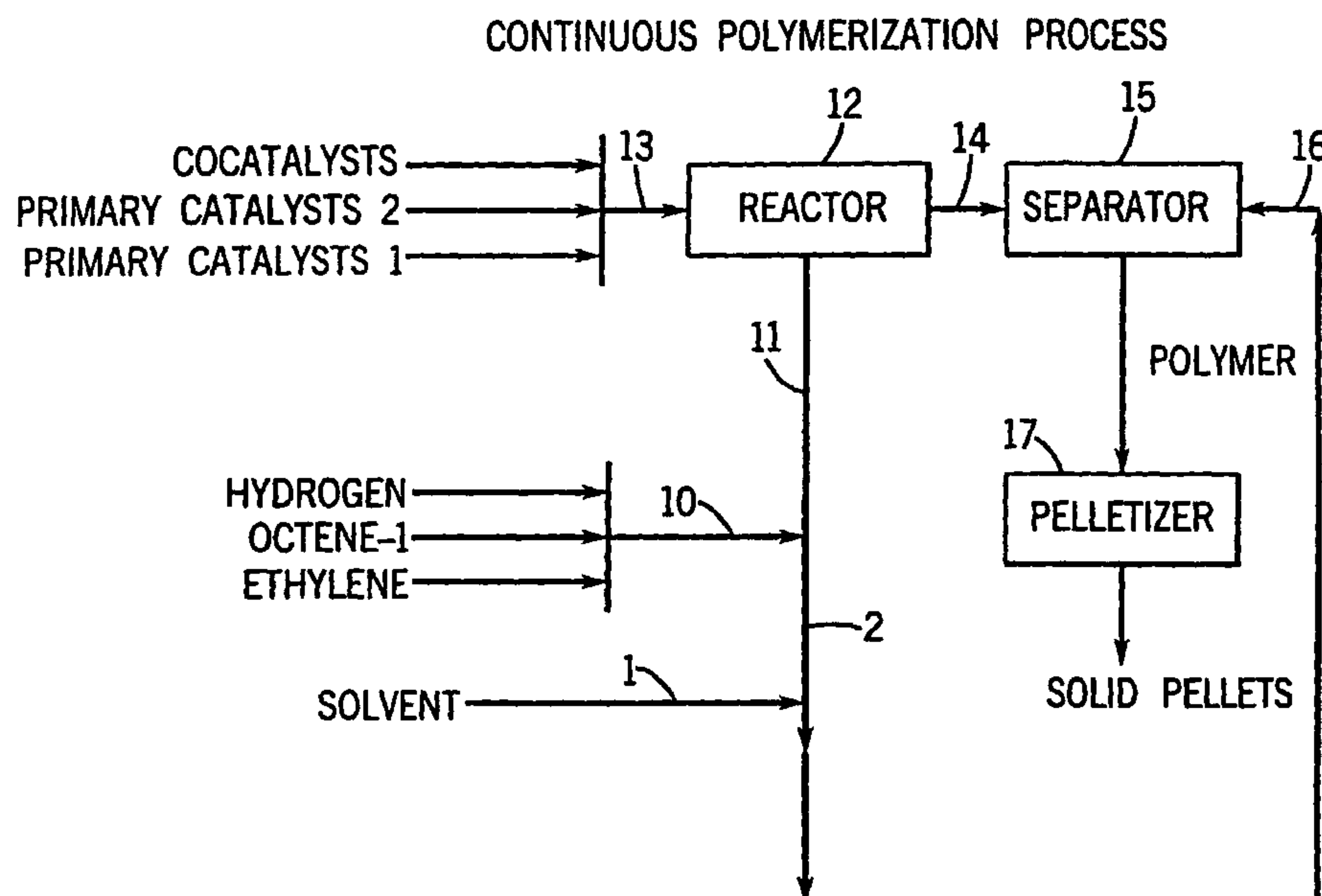
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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **LAUGHNER, Michael, K.** [US/US]; 1403 North Road, Lake Jackson, TX 77566 (US). **MANGOLD, Debra, J.** [US/US]; 301 Juniper Street, Lake Jackson, TX 77566 (US). **PARIKH,**

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(54) Title: PROCESS FOR PREPARING IN A SINGLE REACTOR POLYMER BLENDS HAVING A BROAD MOLECULAR WEIGHT DISTRIBUTION



(57) Abstract: Ethylene-based polymer blends having an MWD of at least 2 were made in a single reactor using a mixed constrained geometry catalyst (CGC) system. The process comprises the steps of contacting under polymerization conditions and in a single reaction vessel (i) ethylene, (ii) at least one C₃-C₂₀α-olefin, (iii) optionally, at least one polyene, and (iv) a mixed CGC system.

**PROCESS FOR PREPARING IN A SINGLE REACTOR POLYMER BLENDS
HAVING A BROAD MOLECULAR WEIGHT DISTRIBUTION**

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This invention relates to polymer blends having a molecular weight distribution (MWD) of at least 2. In one aspect, the invention relates to ethylene/ α -olefin and ethylene/ α -olefin/diene monomer polymer blends, particularly blends useful as elastomers, while in another aspect, the invention relates to a process of preparing such blends in a single reactor. In yet another aspect, the invention relates to a process of making the polymer blends in a single reactor using a mixed constrained geometry catalyst (CGC) system.

Constrained geometry catalysts have found wide acceptance in the manufacture of various olefinic polymers, such as the various ethylene, propylene and diene polymers. These catalysts comprise a metal coordination complex which itself comprises a metal of group 4 of the Periodic Table of the Elements and a delocalized π -bonded moiety substituted with a constrain-inducing moiety, the complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted π -bonded moiety and the center of at least one remaining substituent was less than such angle in a similar complex containing a similar π -bonded moiety lacking in such constrain-inducing substituent. The catalyst further comprises a cocatalyst and an activator. "Delocalized π -bonded moiety" means an unsaturated organic moiety, such as those comprising ethylenic or acetylenic functionality, in which the π -electrons were donated to the metal to form a bond.

The metal atom was the active site of each discreet CGC unit and since each such unit has a single metal atom, these catalysts tend to produce in a highly efficient manner high molecular weight (for example, greater than 10,000 weight average molecular weight) olefin polymers with a narrow MWD (for example, 2 or less) over a wide range of polymerization conditions. CGCs were especially useful for the formation of ethylene homopolymers, copolymers of ethylene and one or more α -olefins (that is, olefins having three or more carbon atoms with the ethylenic unsaturation between the first and second carbon atoms), and interpolymers of ethylene, propylene and a diene monomer (for example, EPDM terpolymers).

While a narrow MWD can impart useful properties to ethylene-based polymers for certain applications, for example, transparency in films, ethylene-based polymers with a broad MWD (for example, greater than 2) usually process more efficiently and have better physical properties, for example, temperature performance, for such applications as
5 injection molded or extruded articles, for example, gaskets and wire and cable coatings, than do ethylene-based polymers with a narrow MWD. Various processes were known for producing broad MWD ethylene-based polymers or polymer blends with a CGC, but all were subject to improvement.

For example, one process for producing such polymers or polymer blends requires
10 the use of multiple reactors deployed in parallel with each reactor containing the same CGC but operated under different polymerization conditions. The product outputs of the reactors were then blended with one another. This produces a polymer blend with a substantially uniform molecular architecture, which was often a desirable property, particularly for elastomers (that is, polymers with a crystallinity of less than 45 percent).
15 For polymer blends of similar crystallinity, those blends of substantially uniform molecular architecture generally exhibit superior physical performance properties, for example, tensile, modulus, tear, etc., than those blends of a relatively nonuniform molecular architecture. "Substantially uniform molecular architecture" means that each polymer molecule of the blend has substantially the same comonomer content and
20 distribution although the polymer molecules from one reactor differ in weight average molecular weight (Mw) from the polymer molecules produced in the other reactor(s).

One difficulty with this process was that it requires balancing the operation and output of one reactor with the other reactor(s). Another difficulty was that it requires a separate, post-reaction blending step. Yet another difficulty was that with the use of
25 multiple reactors, the ratio of high molecular weight (Mw) to low Mw components in the polymer blend was limited to the capacity of each reactor.

In another process, multiple reactors were deployed in series with each reactor operated at substantially the same polymerization conditions but with each reactor containing a different CGC. The output of the first reactor becomes, of course, a feed for
30 the second reactor, and the product output of the second reactor was a polymer blend. While this process avoids the need for a post-reaction blending step, it still requires balancing the operation of one reactor with the other reactor(s) in the series, and the

output of the process was limited by the capacity of the reactors. Moreover, this process often produces a blend in which the molecular architecture was not uniform.

Variations on both of these multiple reactor processes were known, for example, operating the multiple reactors deployed in series at dissimilar conditions, using a catalyst other than or in addition to a CGC, etc., and USP 5,844,045 to Kolthammer and Cardwell, provides a representative description of a multiple reactor process. However, producing a polymer blend in a single reactor, that is, a reactor blend, saves all the costs associated with running multiple reactors. Moreover, the ratio of high molecular weight (Mw) to low Mw components in the polymer blend can be controlled by controlling the weight ratio of one catalyst to another, and thus the capacity of the individual reactors was not a constraining consideration with respect to this property.

For example, USP 4,937,299 to Ewen and Welborn teaches a process for producing (co)polyolefin reactor blends comprising polyethylene and copolyethylene- α -olefins. These blends were prepared in a single reactor by simultaneously polymerizing ethylene and copolymerizing ethylene and an α -olefin in the presence of at least two different metallocenes and an alumoxane. However, Ewen and Welborn do not teach (i) the use of mixed CGC catalyst systems, or (ii) producing an ethylene-based polymer blend having an MWD (a) of at least 2, and (b) at least ten percent greater than either ethylene-based polymer component of the blend prepared in a single reactor with any single component of the mixed catalyst system under similar polymerization conditions. Ewen and Welborn also do not teach the production of an ethylene-based polymer blend in which each polymer component of the blend has a uniform molecular architecture (at least with respect to the polymer units derived from ethylene and the α -olefin).

USP 5,359,015 to Jejelowo teaches a process of producing polyolefins having a controllable broaden MWD utilizing transition metal metallocene catalyst systems comprising a first component comprising at least one transition metal metallocene having at least one cyclopentadienyl ring that was substituted with a first substituent having a secondary or tertiary carbon atom through which it was covalently bonded to the at least one cyclopentadienyl ring in the system, a second component comprising at least one transition metal metallocene having at least one cyclopentadienyl ring that was substituted with a second substituent that was hydrogen or optionally a second hydrocarbon substituent different from the first substituent, and an activator selected from ionic activators or alumoxane or a combination of the two. The MWD of the polymer produced

by the catalyst system was generally somewhere between the high and low MWD that such catalyst system components would produce if utilized alone.

USP 5,627,117 to Mukaiyama and Oouchi teaches a process for producing a polyolefin with a wide MWD, the process employing an olefin polymerization catalyst comprising a transition metal compound having at least two transition metals in which at least one of the metals was bonded to a ligand having a cyclopentadienyl skeleton at least one of the metals was Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and lanthanoid metals and the other was a selected transition metal.

WO 93/13143 to Parikh, Cardwell and Kolthammer teaches a process of producing an interpolymer product comprising a first homogeneous ethylene/ α -olefin interpolymer and at least one-second ethylene/ α -olefin interpolymer. The process comprises the step of using at least two CGCs having different reactivities such that the first ethylene/ α -olefin interpolymer has a narrow MWD with a very high comonomer content and a high molecular weight and the second ethylene/ α -olefin interpolymer also has a narrow MWD but a low comonomer content and a molecular weight lower than that of the first interpolymer. The first and second ethylene/ α -olefin interpolymers can be polymerized in a single reactor.

WO 99/31147 to Nemzek, Karol and Kao teaches a gas phase ethylene polymerization process which uses a mixed catalyst system comprising at least one supported and at least one unsupported metallocene catalyst. The metallocene catalysts include CGCs, the polymerization process can be conducted in a single reaction vessel, and the process produces a polymer blend. However, none of the polymer blends reported in the examples have an MWD greater than any of the polymer components of the blend, and the molecular architecture of the blend polymer components was unreported.

None of these references, the U.S. patents teach the use of a mixed CGC system to produce a reactor blend (i) having an MWD (a) of at least 2, and (b) at least ten percent greater than either ethylene-based polymer component of the blend prepared in a single reactor with any single component of the mixed catalyst system under similar polymerization conditions, and (ii) in which each polymer component of the blend has a uniform molecular architecture (at least with respect to the polymer units derived from ethylene and the α -olefin).

According to one embodiment of this invention, an ethylene-based polymer blend (i) having an MWD (a) of at least 2, and (b) at least ten percent greater than any ethylene-based polymer component of the blend prepared in a single reactor with any single component of the mixed catalyst system under similar polymerization conditions, and (ii) in which each polymer component of the blend has a uniform molecular architecture (at least with respect to the polymer units derived from ethylene and the α -olefin) was prepared by contacting under polymerization conditions and in a single reaction vessel:

- A. ethylene,
- B. at least one C_3 - C_{20} α -olefin, and
- 10 C. a mixed CGC system comprising a first catalyst and a second catalyst, each catalyst having substantially the same reactivity ratio and each catalyst comprising:

- 1. A metal complex of formula I



wherein M was a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4 bound in an η^5 bonding mode to L;

L was a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least the divalent moiety, Z, and L further may be substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino or silyl groups containing up to 20 nonhydrogen atoms;

25 Z was a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

X was an anionic ligand group having up to 60 atoms exclusive of the class of ligands that were cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence was a neutral ligating compound having up to 20 atoms;

p was 0, 1 or 2, and was two less than the formal oxidation state of M, with the proviso that when X was a dianionic ligand group, p was 1; and

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q was 0, 1 or 2; and

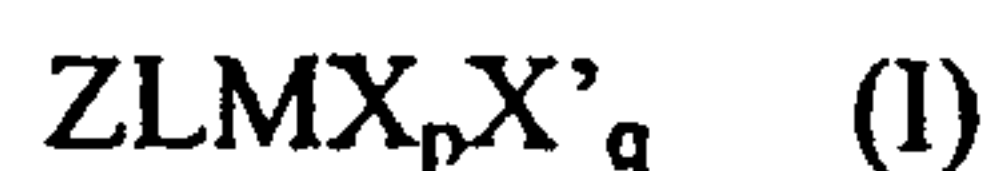
2. An activating cocatalyst;

with the provisos that (i) the first catalyst was different from the second catalyst, (ii) the first catalyst has a reactivity ratio that was substantially the same as the reactivity ratio of the second catalyst with respect to ethylene and the at least one C₃-C₂₀ α-olefin, and (iii) the weight ratio of the first catalyst to the second catalyst, based on the weight of the metal M in each catalyst, was between 90:10 and 10:90.

In another embodiment of the invention, an ethylene-based polymer blend having an MWD (a) of at least 2, and (b) at least ten percent greater than any ethylene-based polymer component of the blend prepared in a single reactor with any single component of the mixed catalyst system under similar polymerization conditions was prepared by contacting under polymerization conditions and in a single reaction vessel:

- A. ethylene,
- B. at least one C₃-C₂₀ α-olefin,
- C. at least one polyene, and
- D. a mixed CGC system comprising a first catalyst and a second catalyst, each catalyst having substantially the same reactivity ratio and each catalyst comprising:

- 1. A metal complex of formula I,



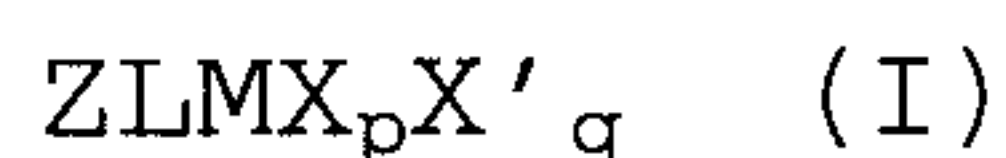
and

- 2. an activating cocatalyst;

with the provisos that (i) the first catalyst was different from the second catalyst, and (ii) the weight ratio of the first catalyst to the second catalyst, based on the weight of the metal M in each catalyst, was between 90:10 and 10:90. The definition of Z, L, M, X, X', p and q were as defined above.

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According to one aspect of the present invention, there is provided an ethylene-based polymer blend having (a) a molecular weight distribution (i) of at least 2, and (ii) at least ten percent greater than that of a polymer prepared in a single reactor with either the first or second catalyst alone under similar polymerization conditions, and (b) a uniform molecular architecture, the polymer blend prepared by a process comprising contacting under polymerization conditions and in a single reaction vessel: A. ethylene, B. at least one C₃-C₂₀ α -olefin, and C. a mixed catalyst system comprising a first catalyst and a second catalyst, and each catalyst comprising: 1. a metal complex of formula I



wherein M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4 bound in an η^5 bonding mode to L; L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least the divalent moiety, Z, and L further may be substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino and silyl groups containing up to 20 nonhydrogen atoms; Z is a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen; X is an anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups; X' independently in each occurrence is a neutral ligating

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compound having up to 20 atoms; p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that when X is a dianionic ligand group, p is 1; and q is 0, 1 or 2; and 2. an activating cocatalyst; with the provisos
 5 that D. the first catalyst is different from the second catalyst, and E. the weight ratio of the first catalyst to the second catalyst, based on the weight of the metal M in each catalyst, is between 90:10 and 10:90.

According to another aspect of the present
 10 invention, there is provided an ethylene-based polymer blend having an MWD (a) of at least 2, and (b) at least ten percent greater than any ethylene-based polymer component of the blend prepared in a single reactor with any single component of the mixed catalyst system under similar
 15 polymerization conditions, and (b) a uniform molecular architecture, the polymer blend prepared by a process comprising contacting under polymerization conditions and in a single reaction vessel: A. ethylene, B. at least one C₃-C₂₀ α-olefin, C. at least one polyene, and D. a mixed
 20 constrained geometry catalyst (CGC) system comprising a first catalyst and a second catalyst, each catalyst having substantially the same reactivity ratio with respect to at least one C₃-C₂₀ α-olefin of B, and each catalyst comprising:
 1. A metal complex of formula I,



wherein M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4 bound in an η^5 bonding mode to L; L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-,
 30 tetrahydrofluorenyl-, or octahydrofluorenyl-group covalently substituted with at least the divalent moiety, Z, and L further may be substituted with from 1 to 8 substituents

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independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino and silyl groups containing up to 20 nonhydrogen atoms; Z is a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen; X is an anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups; X' independently in each occurrence is a neutral ligating compound having up to 20 atoms; p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that when X is a dianionic ligand group, p is 1; and q is 0, 1 or 2; and 2. an activating cocatalyst; with the provisos that E. the first catalyst is different from the second catalyst, and F. the weight ratio of the first catalyst to the second catalyst, based on the weight of the metal M in each catalyst, is between 90:10 and 10:90.

According to yet another aspect of the present invention, there is provided an article made from the polymer blend described herein.

In both embodiments, the polymer blend may be recovered from the reaction vessel in any convenient manner.

Each CGC of the system produces an ethylene/ α -olefin polymer that has substantially the same molecular architecture as the ethylene/ α -olefin polymer produced by the other CGC of the system, but each polymer has a different molecular weight. The reaction temperature controls the molecular weights of the copolymers. With respect to

ethylene/ α -olefin/polyene polymer blends, the molecular architecture of a polymer produced by one CGC of the system may differ from the molecular architecture of a polymer produced by the other CGC of the system because the reactivity ratio of the polyene may be different with each CGC of the system (although the size and distribution of the ethylene runs in each polymer molecule may be substantially similar).

The polymer blend also has a rheology ratio greater than any ethylene-based polymer component of the blend prepared in a single reactor with any single component of the mixed catalyst system under similar polymerization conditions.

By "mixed catalyst system" was meant that each CGC of the system was different from the other CGC. The CGCs can differ in one or more of their respective constituent parts, that is, the metal and/or organic ligand component of the metal complex, the cocatalyst and the activator. The mixed catalyst system can comprise two or more CGCs, but dual systems (that is, systems containing essentially only two CGCs) were preferred.

FIG. 1 was a flow diagram illustrating a continuous polymerization process for the production of a polymer blend in a single reaction vessel using a mixed catalyst system.

FIG. 2 was a viscosity shear rate curve at 190 C reporting the superior processability of 30 Mooney ethylene/1-octene elastomer blend made with a dual GCG system as compared to elastomers made with only one component of the dual CGC system.

FIG. 3 was Gottfert Rheotens Data at 190 C reporting the superior melt strength of 30 Mooney ethylene/1-octene elastomer blend made with a dual GCG system as compared to an elastomer made with only one component of the dual CGC system.

The blend components of this invention were either homopolymers of ethylene ($\text{CH}_2=\text{CH}_2$) or polymers, that is, interpolymers, of ethylene with at least one $\text{C}_3\text{-C}_{20}$ α -olefin (preferably an aliphatic α -olefin) comonomer, and/or a polyene comonomer, for example, a conjugated diene, a nonconjugated diene, a triene, etc. The term interpolymers includes copolymers, for example ethylene/propylene (EP), and terpolymers, for example EPDM, but it was not limited to polymers made with only ethylene and one or two monomers. Examples of the $\text{C}_3\text{-C}_{20}$ α -olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. The α -olefin can also contain a cyclic structure such as

cyclohexane or cyclopentane, resulting in an α -olefin such as 3-cyclohexyl-1-propene (allyl-cyclohexane) and vinyl-cyclohexane. Although not α -olefins in the classical sense of the term, for purposes of this invention certain cyclic olefins, such as norbornene and related olefins, were α -olefins and can be used in place of some or all of the α -olefins
5 described above. Similarly, styrene and its related olefins (for example, α -methylstyrene, etc.) were α -olefins for purposes of this invention.

Polyenes were unsaturated aliphatic or alicyclic compounds containing more than four carbon atoms in a molecular chain and having at least two double and/or triple bonds, for example, conjugated and nonconjugated dienes and trienes. Examples of
10 nonconjugated dienes include aliphatic dienes such as 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,5-hexadiene, 1,6-heptadiene, 6-methyl-1,5-heptadiene, 1,6-octadiene, 1,7-octadiene, 7-methyl-1,6-octadiene, 1,13-tetradecadiene, 1,19-eicosadiene, and the like; cyclic dienes such as 1,4-cyclohexadiene, bicyclo[2.2.1]hept-2,5-diene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene,
15 bicyclo[2.2.2]oct-2,5-diene, 4-vinylcyclohex-1-ene, bicyclo[2.2.2]oct-2,6-diene, 1,7,7-trimethylbicyclo-[2.2.1]hept-2,5-diene, dicyclopentadiene, methyltetrahydroindene, 5-allylbicyclo[2.2.1]hept-2-ene, 1,5-cyclooctadiene, and the like; aromatic dienes such as 1,4-diallylbenzene, 4-allyl-1H-indene; and trienes such as 2,3-diisopropenylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene, 2-propenyl-2,5-norbornadiene,
20 1,3,7-octatriene, 1,4,9-decatriene, and the like; with 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene and 7-methyl-1,6-octadiene preferred nonconjugated dienes.

Examples of conjugated dienes include butadiene, isoprene, 2,3-dimethylbutadiene-1,3, 1,2-dimethylbutadiene-1,3, 1,4-dimethylbutadiene-1,3, 1-ethylbutadiene-1,3, 2-phenylbutadiene-1,3, hexadiene-1,3, 4-methylpentadiene-1,3, 1,3-
25 pentadiene ($\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$; commonly called piperylene), 3-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 3-ethyl-1,3-pentadiene, and the like; with 1,3-pentadiene a preferred conjugated diene.

Examples of trienes include 1,3,5-hexatriene, 2-methyl-1,3,5-hexatriene, 1,3,6-heptatriene, 1,3,6-cycloheptatriene, 5-methyl-1,3,6-heptatriene, 5-methyl-1,4,6-
30 heptatriene, 1,3,5-octatriene, 1,3,7-octatriene, 1,5,7-octatriene, 1,4,6-octatriene, 5-methyl-1,5,7-octatriene, 6-methyl-1,5,7-octatriene, 7-methyl-1,5,7-octatriene, 1,4,9-decatriene and 1,5,9-cyclodecatriene.

Polymer blends comprising copolymers of ethylene and one aliphatic C₃-C₂₀ α-olefin or one polyene (either conjugated or nonconjugated) can be prepared using the process of this invention. Polymer blends comprising interpolymers of ethylene, at least one aliphatic C₃-C₂₀ α-olefin, and/or at least one polyene (either conjugated or nonconjugated) can also be made by using this process. Exemplary copolymers include ethylene/propylene, ethylene/butene, ethylene/1-octene, ethylene/5-ethylidene-2-norbornene, ethylene/5-vinyl-2-norbornene, ethylene/-1,7-octadiene, ethylene/7-methyl-1,6-octadiene and ethylene/1,3,5-hexatriene. Exemplary terpolymers include ethylene/propylene/1-octene, ethylene/butene/1-octene, ethylene/propylene/5-ethylidene-2-norbornene, ethylene/butene/5-ethylidene-2-norbornene, ethylene/butene/styrene, ethylene/1-octene/5-ethylidene-2-norbornene, ethylene/propylene/1,3-pentadiene, ethylene/propylene/7-methyl-1,6-octadiene, ethylene/butene/7-methyl-1,6-octadiene, ethylene/1-octene/1,3-pentadiene and ethylene/propylene/1,3,5-hexatriene. Exemplary tetrapolymers include ethylene/propylene/1-octene/diene (for example ENB), ethylene/butene/1-octene/diene and ethylene/propylene/mixed dienes, for example ethylene/propylene/5-ethylidene-2-norbornene/piperylene. In addition, the blend components made using the process of this invention can include minor amounts, for example 0.05-0.5 percent by weight, of long chain branch enhancers, such as 2,5-norbornadiene (aka bicyclo[2,2,1]hepta-2,5-diene), diallylbenzene, 1,7-octadiene (H₂C=CH(CH₂)₄CH=CH₂), and 1,9-decadiene (H₂C=CH(CH₂)₆CH=CH₂).

Typically, the blend components made by the process of this invention comprise at least 20, preferably at least 30 and more preferably at least 40, weight percent ethylene; at least 5, preferably at least 15 and more preferably at least 25, weight percent of at least one α-olefin; and, if a polyene-containing terpolymer, greater than 0, preferably at least 0.1 and more preferably at least 0.5, weight percent of at least one conjugated or nonconjugated polyene. As a general maximum, the blend components made by the process of this invention comprise not more than 95, preferably not more than 85 and more preferably not more than 75, weight percent ethylene; not more than 80, preferably not more than 70 and more preferably not more than 60, weight percent of at least one α-olefin; and, if a terpolymer, not more than 20, preferably not more than 15 and more preferably not more than 12, weight percent of at least one of a conjugated or nonconjugated diene. All weight percentages were based on weight of the blend.

The polydispersity (molecular weight distribution or Mw/Mn or MWD) of the polymer blend generally ranges from at least 2, preferably at least 2.1, and especially at least 2.2 to 10, preferably 6, and especially 4. One hallmark of this invention was that the MWD of the polymer blend was at least 10, preferably at least 15 and more preferably at least 20, percent greater than a polymer blend component prepared in a single reaction vessel with either the first or second catalyst alone under similar polymerization conditions.

The polydispersity index was typically measured by gel permeation chromatography (GPC) on a Waters 150 C high temperature chromatographic unit equipped with three linear mixed bed columns (Polymer Laboratories (10 micron particle size)) operating at a system temperature of 140 C. The solvent was 1,2,4-trichlorobenzene from which 0.5 percent by weight solutions of the samples were prepared for injection. The flow rate was 1.0 milliliter/minute, and the injection size was 100 microliters.

The molecular weight determination was deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights were determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to derive the equation:

$$M_{\text{polyethylene}} = (a) (M_{\text{polystyrene}})^b$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, Mw, was calculated in the usual manner according to the formula:

$$M_w = \sum(w_i)(M_i)$$

where w_i and M_i were the weight fraction and molecular weight respectively of the i^{th} fraction eluting from the GPC column. Generally, the Mw of the polymer blend ranges from 10,000, preferably 20,000, more preferably 40,000, and especially 60,000, to 1,000,000, preferably 800,000, more preferably 600,000, and especially 500,000.

The polymer blends made by the process of this invention cover a range of viscosities, depending upon the molecular weight of the blend and optional post-

polymerization rheological modification. In general, the blend viscosity was characterized by a Mooney viscosity which was measured according to ASTM D 1646-89 using a shear rheometer at 125 C. The polymer blend Mooney viscosity generally ranges from a minimum of less than 0.01, preferably 0.1, more preferably 1, and especially 15 to
5 a maximum of 150, preferably 125, more preferably 100, and especially 80.

The rheological or shear thinning behavior of the ethylene interpolymer was determined by measuring the ratio of interpolymer viscosity at 0.1 rad/sec to viscosity at 100 rad/sec. This ratio was known as the Rheology Ratio (RR), $V_{0.1}/V_{100}$, or more simply, 0.1/100. The RR was an extension of I_{10}/I_2 and as such, in those instances in
10 which the measurement of I_2 and I_{10} were difficult, for example, the I_2 was less than 0.5, or the molecular weight of the interpolymer was relatively high, or the Mooney viscosity of the interpolymer was greater than 35, the RR of the interpolymer can be measured using a parallel plate rheometer. One hallmark of this invention was that the rheology ratio of the polymer blend was typically greater than that of a polymer blend component
15 of substantially the same Mooney viscosity and prepared in a single reaction vessel with either the first or second catalyst alone under similar polymerization conditions.

The density of the polymer blends was measured according to ASTM D-792, and this density ranges from a minimum of 0.850 grams/cubic centimeter (g/cm^3), preferably 0.853 g/cm^3 , and especially 0.855 g/cm^3 , to a maximum of 0.970 g/cm^3 , preferably 0.940
20 g/cm^3 , and especially 0.930 g/cm^3 . For those polymer blends that were elastomers, that is, with a crystallinity less than 45 percent, the maximum density was 0.895, preferably 0.885 and more preferably 0.875, g/cm^3 .

For polymer blends intended for use as elastomers, the crystallinity was preferably less than 40, more preferably less than 30, percent, preferably in combination with a
25 melting point of less than 115, preferably less than 105, C, respectively. Elastomeric polymer blends with a crystallinity of 0 to 25 percent were even more preferred. The percent crystallinity was determined by dividing the heat of fusion as determined by differential scanning calorimetry (DSC) of a polymer blend sample by the total heat of fusion for that polymer blend sample. The total heat of fusion for high-density
30 homopolymer polyethylene (100 percent crystalline) was 292 joule/gram (J/g).

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Mixed Catalyst System

The constrained geometry metal complexes of the mixed catalyst system, and methods for their preparation, were disclosed in U.S.S.N. 545,403 filed July 3, 1990 (EP-A-416,815); EP-A-514,828; USP 5,721,185 and USP 5,374,696; as well as USP 5,470,993, 5,374,696, 5,231,106, 5,055,438, 5,057,475, 5,096,867, 5,064,802, 5,132,380, 5,321,106, 5,470,993, 5,486,632, WO 95/00526, and WO 98/49212 and. In EP-A-514,828 certain borane derivatives of the foregoing catalysts were disclosed and a method for their preparation taught and claimed. In USP 5,453,410 combinations of cationic catalyst complexes with an alumoxane were disclosed as suitable olefin polymerization catalysts. Various substituted indenyl containing metal complexes are taught in WO 95/14024.

The CGCs used in the practice of this invention comprise:

- A. 1) a metal complex of formula (I), and
2) an activating cocatalyst,
the metal complex and the activating cocatalyst present in a molar ratio of 1:10,000 to 100:1, or
B. the reaction product formed by converting a metal complex of formula (I) to an active catalyst by use of an activating technique.

Formula (I) is:



wherein M was a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4 bound in an η^5 bonding mode to L;

L was a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least the divalent moiety, Z, and L further may be substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino or silyl groups containing up to 20 nonhydrogen atoms;

Z was a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, Z comprising boron, or a

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member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

X was an anionic ligand group having up to 60 atoms exclusive of the class of ligands that were cyclic, delocalized, π -bound ligand groups;

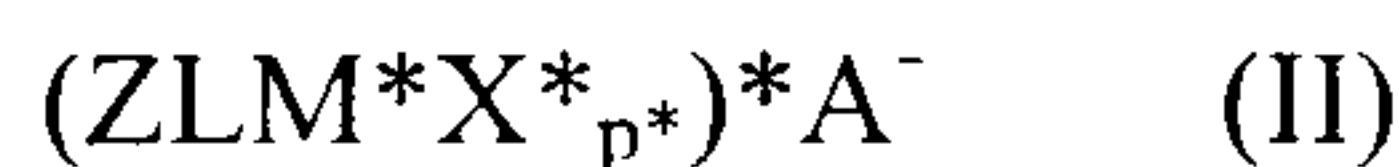
5 X' independently each occurrence was a neutral ligating compound having up to 20 atoms;

p was 0, 1 or 2, and was two less than the formal oxidation state of M, with the proviso that when X was a dianionic ligand group, p was 1; and

q was 0, 1 or 2.

10 The metal complex of formula I was rendered catalytically active by combination with an activating cocatalyst or use of an activating technique.

In one embodiment, the metal complex was of formula II



15 wherein: M* was a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +3 or +4, bound in an η^5 bonding mode to L;

L was a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least the divalent moiety, Z. and L further may be substituted with from 1 to 4 substituents
20 independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, dihydrocarbylphosphino or silyl groups containing up to 20 nonhydrogen atoms;

Z was a divalent moiety bound to both L and M* via σ -bonds, Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also
25 optionally comprising nitrogen, phosphorus, sulfur or oxygen;

X* was an anionic ligand group having up to 60 atoms exclusive of the class of ligands that were cyclic, delocalized, π -bound ligand groups;

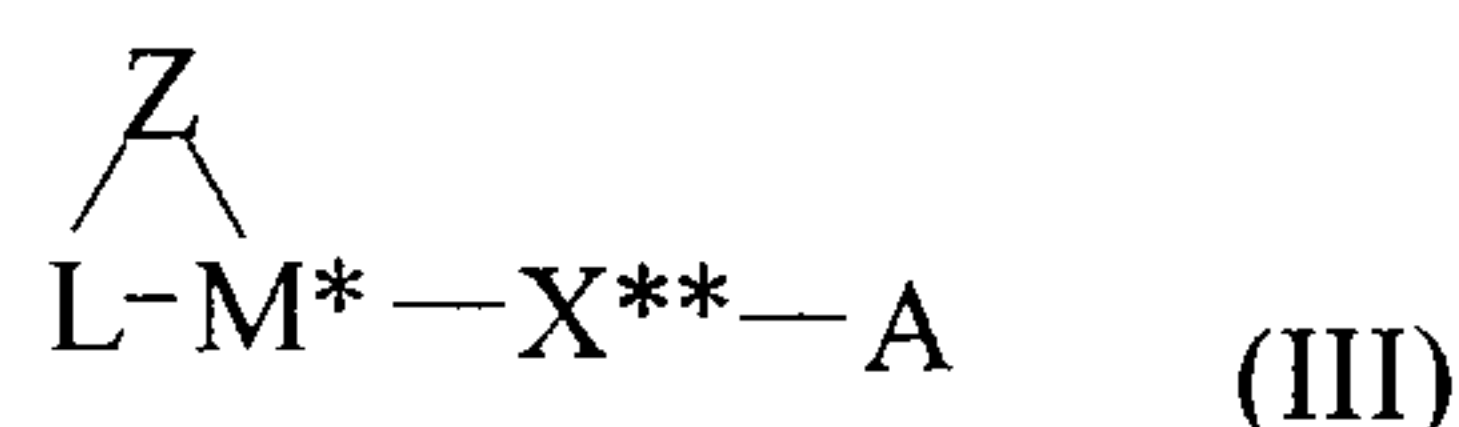
p* was 0 or 1, and was three less than the formal oxidation state of M; and

A⁻ was an inert, noncoordinating anion.

30 All reference to the Periodic Table of the Elements shall refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1995. Also, any

reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

Zwitterionic complexes result from activation of a Group 4 metal diene complex, that is, complexes in the form of a metallocyclopentene wherein the metal was in the +4 formal oxidation state, by the use of a Lewis acid activating cocatalyst, especially tris(perfluoroaryl)borane compounds. These zwitterionic complexes were believed to correspond to formula (III):



10

M was a Group 4 metal in the +4 formal oxidation state;

L and Z were as previously defined;

X** was the divalent remnant of the conjugated diene formed by ring opening at one of the carbon to metal bonds of a metallocyclopentene; and

15

A was the moiety derived from the activating cocatalyst.

20

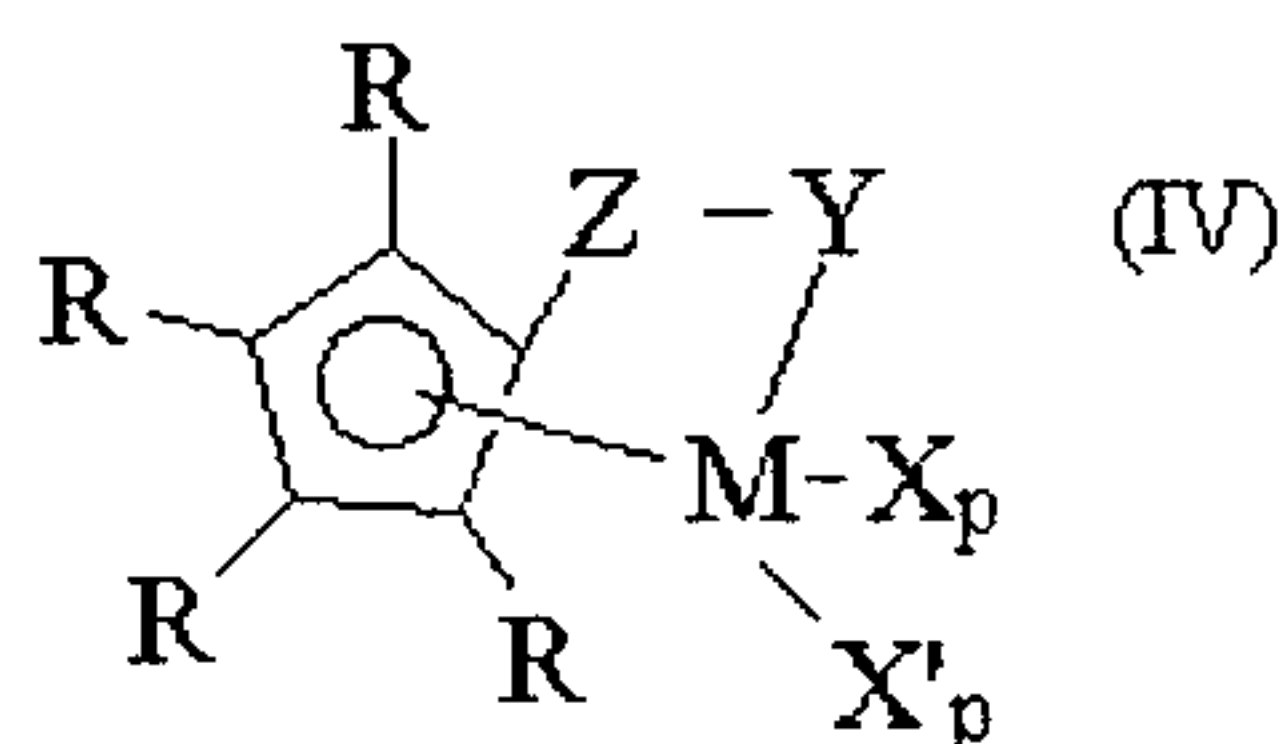
As used herein, "noncoordinating, compatible anion" means an anion which either does not coordinate to component A) or which was only weakly coordinated with A) and remains sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating, compatible anion specifically refers to a compatible anion which when functioning as a charge balancing anion in one of the CGCs of dual CGC system, does not transfer an anionic substituent or fragment of the substituent to the cation to form a neutral four coordinate complex and a neutral metal byproduct. "Compatible anions" were anions which were not degraded to neutrality when the initially formed complex decomposes and were noninterfering with desired subsequent polymerizations.

25

Preferred X' groups were phosphines, especially trimethylphosphine, triethylphosphine, triphenylphosphine and bis(1,2-dimethylphosphino)ethane; P(OR^{iv})₃, wherein R^{iv} was a hydrocarbyl group preferably containing 1 to 20 carbon atoms; ethers, especially tetrahydrofuran; amines, especially pyridine, bipyridine, tetramethylethylenediamine (TMEDA), and triethylamine; olefins, and conjugated dienes having from 4 to 40 carbon atoms. Complexes including the latter X' groups include those in which the metal was in the +2 formal oxidation state.

30

In one preferred embodiment, A) metal complexes used according to the present invention were complexes corresponding to formula (IV):



5 in which:

R independently each occurrence was a group selected from hydrogen, hydrocarbyl, halohydrocarbyl, silyl, germyl and mixtures thereof, said group containing up to 20 nonhydrogen atoms;

M was titanium, zirconium or hafnium;

10 Z was a divalent moiety comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen, said moiety having up to 60 nonhydrogen atoms;

X and X' were as previously defined;

p was 0, 1 or 2; and

15 q was 0 or 1;

with the proviso that;

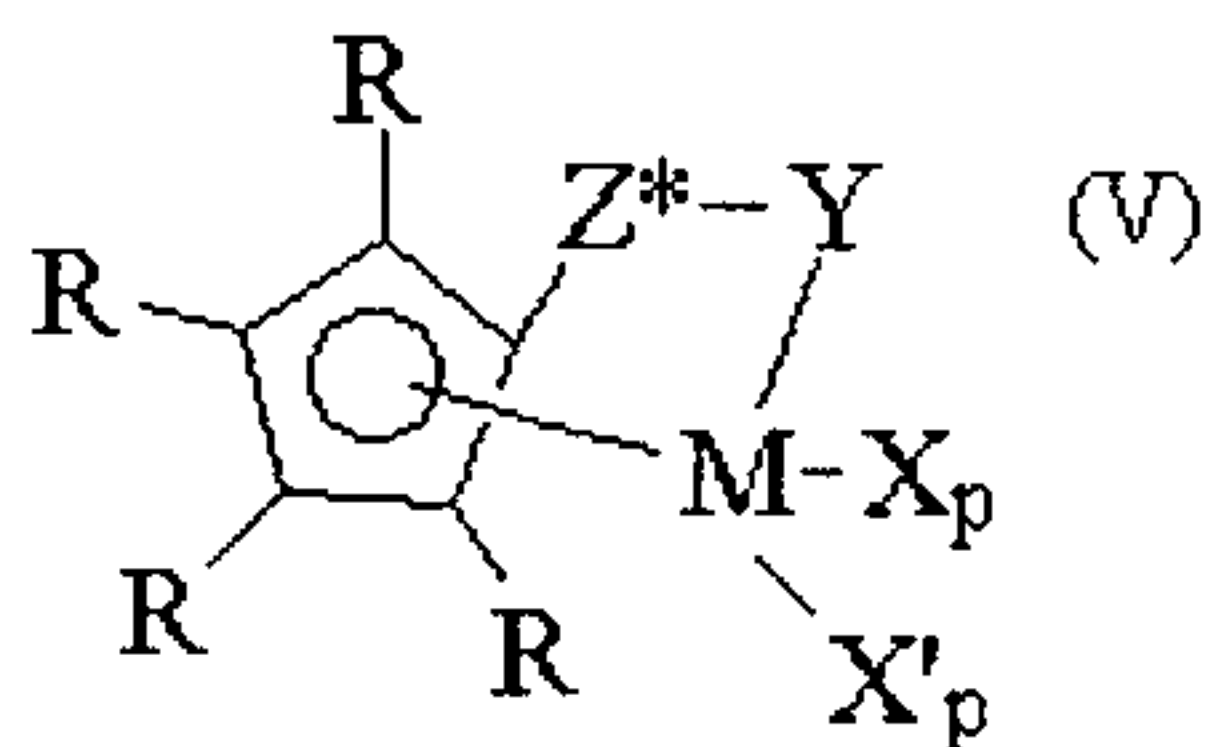
when p was 2, q was 0, M was in the +4 formal oxidation state, and X was an anionic ligand selected from the group consisting of halide, hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, di(hydrocarbyl)phosphido, hydrocarbylsulfido, and silyl groups, as
20 well as halo-, di(hydrocarbyl)amino-, hydrocarbyloxy- and di(hydrocarbyl)phoshino-substituted derivatives thereof, said X group having up to 20 nonhydrogen atoms,

when p was 1, q was 0, M was in the +3 formal oxidation state, and X was a stabilizing anionic ligand group selected from the group consisting of allyl, 2-(N,N-dimethylaminomethyl)phenyl, and 2-(N,N-dimethyl)aminobenzyl, or M was in the +4
25 formal oxidation state, and X was a divalent derivative of a conjugated diene, M and X together forming a metallocyclopentene group, and

when p was 0, q was 1, M was in the +2 formal oxidation state, and X' was a neutral, conjugated or nonconjugated diene, optionally substituted with one or more hydrocarbyl groups, said X' having up to 40 carbon atoms and forming a π -complex with

30 M.

More preferred A) coordination complexes of this embodiment were complexes corresponding to formula (V):



wherein

5 R independently each occurrence was hydrogen or C₁₋₆ alkyl;

M was titanium;

Y was -O-, -S-, -NR^{*}-, -PR^{*}-;

Z^{*} was SiR^{*}₂, CR^{*}₂, SiR^{*}₂SiR^{*}₂, CR^{*}₂CR^{*}₂, CR^{*}=CR^{*}, CR^{*}₂SiR^{*}₂, or GeR^{*}₂;

10 R^{*} each occurrence was independently hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, and R^{*} having up to 20 nonhydrogen atoms, and optionally, two R^{*} groups from Z (when R^{*} was not hydrogen), or an R^{*} group from Z and an R^{*} group from Y form a ring system;

p was 0, 1 or 2;

15 q was 0 or 1;

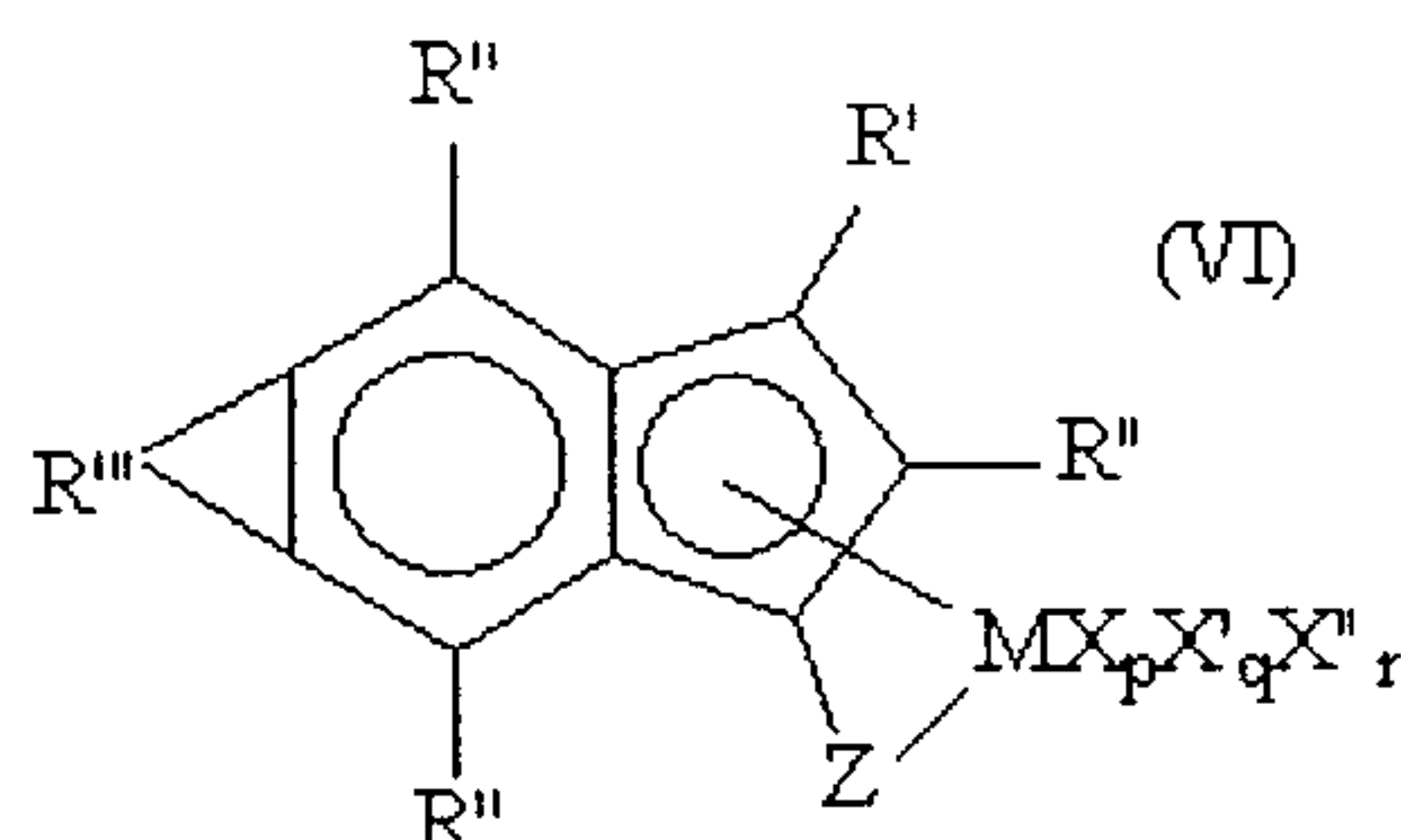
with the proviso that:

when p was 2, q was 0, M was in the +4 formal oxidation state, and X was independently each occurrence methyl or benzyl,

20 when p was 1, q was 0, M was in the +3 formal oxidation state, and X was 2 (N,N-dimethyl)aminobenzyl; or M was in the +4 formal oxidation state and X was 1,4-butadienyl, and

25 when p was 0, q was 1, M was in the +2 formal oxidation state, and X' was 1,4-diphenyl-1,3-butadiene or 1,3-pentadiene. The latter diene was illustrative of unsymmetrical diene groups that result in production of metal complexes that were actually mixtures of the respective geometrical isomers.

In another preferred embodiment, the A) metal complexes used according to the present invention were complexes corresponding to formula (VI):



where M was titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation
 5 state;

R' and R'' were independently each occurrence hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl,
 10 silyl-substituted hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said R' or R'' group having up to 40
 15 nonhydrogen atoms, and optionally two or more of the foregoing groups may together form a divalent derivative;

R''' was a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said R''' containing from 1 to 30 nonhydrogen atoms;

20 Z was a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

X was a monovalent anionic ligand group having up to 60 atoms exclusive of the
 25 class of ligands that were cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence was a neutral ligating compound having up to 20 atoms;

X'' was a divalent anionic ligand group having up to 60 atoms;

p was 0, 1, 2, or 3;

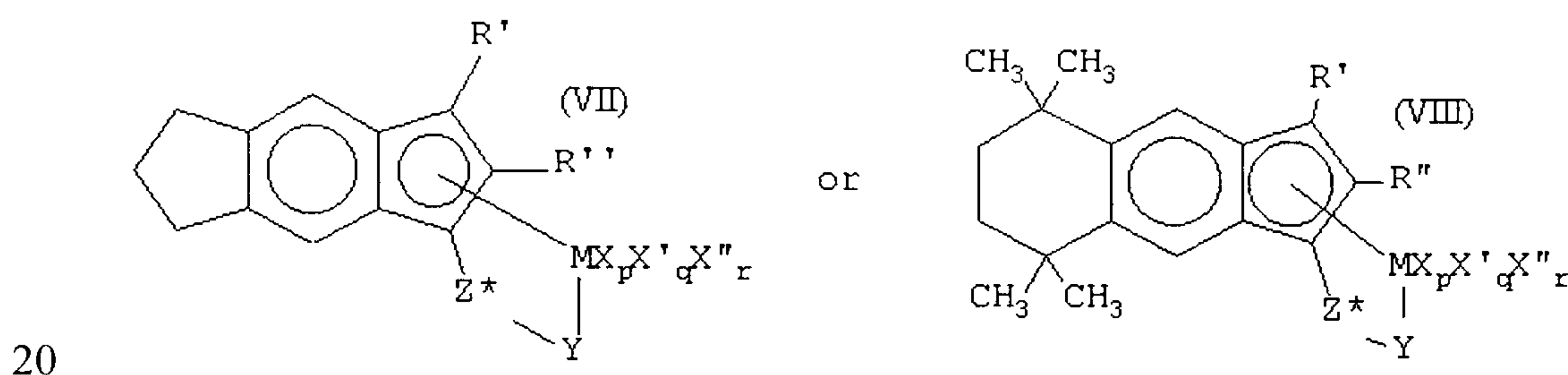
30 q was 0, 1 or 2, and

r was 0 or 1.

The number of X groups depends on the oxidation state of M, whether Z was divalent or not and whether any neutral diene groups or divalent X'' groups were present. The skilled artisan will appreciate that the quantity of the various substituents and the identity of Z were chosen to provide charge balance, thereby resulting in a neutral metal complex. For example, when Z was divalent, and r was 0, p was two less than the formal oxidation state of M. When Z contains one neutral two electron coordinate-covalent bonding site, and M was in a formal oxidation state of +3, p may equal 0 and r equal 1, or p may equal 2 and r equal 0. In a final example, if M was in a formal oxidation state of +2, Z may be a divalent ligand group, p and r may both equal 0 and one neutral ligand group may be present.

The above complexes may exist as isolated crystals optionally in pure form or as a mixture with other complexes, in the form of a solvated adduct, optionally in a solvent, especially an organic liquid, as well as in the form of a dimer or chelated derivative thereof, wherein the chelating agent was an organic material such as ethylenediaminetetraacetic acid (EDTA).

Preferred coordination complexes for use as part of the second component of the dual CGC catalyst system were complexes corresponding to formula (VII) or (VIII):



wherein:

R' was hydrocarbyl, di(hydrocarbylamino), or a hydrocarbyleneamino group, said R' having up to 20 carbon atoms,

25 R'' was C₁₋₂₀ hydrocarbyl or hydrogen;

M was titanium;

Y was -O-, -S-, -NR^{*}-, -PR^{*}-; -NR₂^{*}, or -PR₂^{*};

Z^{*} was SiR^{*}₂, CR^{*}₂, SiR^{*}₂SiR^{*}₂, CR^{*}₂CR^{*}₂, CR^{*}=CR^{*}, CR^{*}₂SiR^{*}₂, or GeR^{*}₂;

R* each occurrence was independently hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R* having up to 20 non-hydrogen atoms, and optionally, two R* groups from Z (when R* was not hydrogen), or an R* group from Z and an R* group from Y form a
5 ring system;

X, X' and X'' were as previously defined;

p was 0, 1 or 2;

q was 0 or 1; and

r was 0 or 1;

10 with the proviso that:

when p was 2, q and r were 0, M was in the +4 formal oxidation state (or M was in the +3 formal oxidation state if Y was -NR*₂ or -PR*₂), and X was an anionic ligand selected from the group consisting of halide, hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, di(hydrocarbyl)phosphido, hydrocarbylsulfido, and silyl groups, as well
15 as halo-, di(hydrocarbyl)amino-, hydrocarbyloxy-, and di(hydrocarbyl)phosphino-substituted derivatives thereof, said X group having up to 30 nonhydrogen atoms,

when r was 1, p and q were 0, M was in the +4 formal oxidation state, and X'' was a dianionic ligand selected from the group consisting of hydrocarbadiyl, oxyhydrocarbyl, and hydrocarbylenedioxy groups, said X group having up to 30 nonhydrogen atoms,

20 when p was 1, q and r were 0, M was in the +3 formal oxidation state, and X was a stabilizing anionic ligand group selected from the group consisting of allyl, 2-(N,N-dimethylamino)phenyl, 2-(N,N-dimethylaminomethyl)phenyl, and 2-(N,N-dimethylamino)benzyl, and

when p and r were 0, q was 1, M was in the +2 formal oxidation state, and X' was
25 a neutral, conjugated or nonconjugated diene, optionally substituted with one or more hydrocarbyl groups, said X' having up to 40 carbon atoms and forming a π -complex with M. Most preferred metal complexes were those according to the previous formula (XIV) or (XV), wherein M, X, X', X'', R' R'', Z*, Y, p, q and r were as previously defined, with the proviso that:

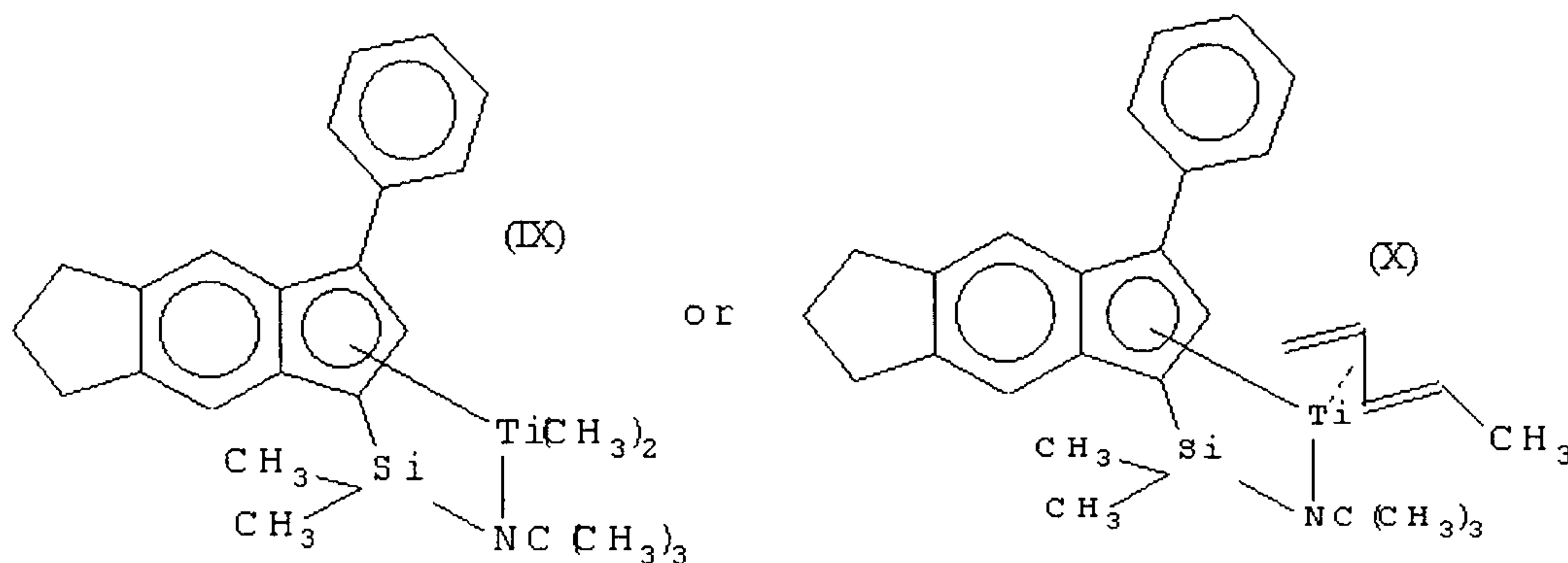
30 when p was 2, q and r were 0, M was in the +4 formal oxidation state, and X was independently each occurrence methyl, benzyl, or halide;

when p and q were 0, r was one, and M was in the +4 formal oxidation state, X'' was a 1,4-butadienyl group that forms a metallocyclopentene ring with M,

when p was 1, q and r were 0, M was in the +3 formal oxidation state, and X was 2-(N,N-dimethylamino)benzyl; and

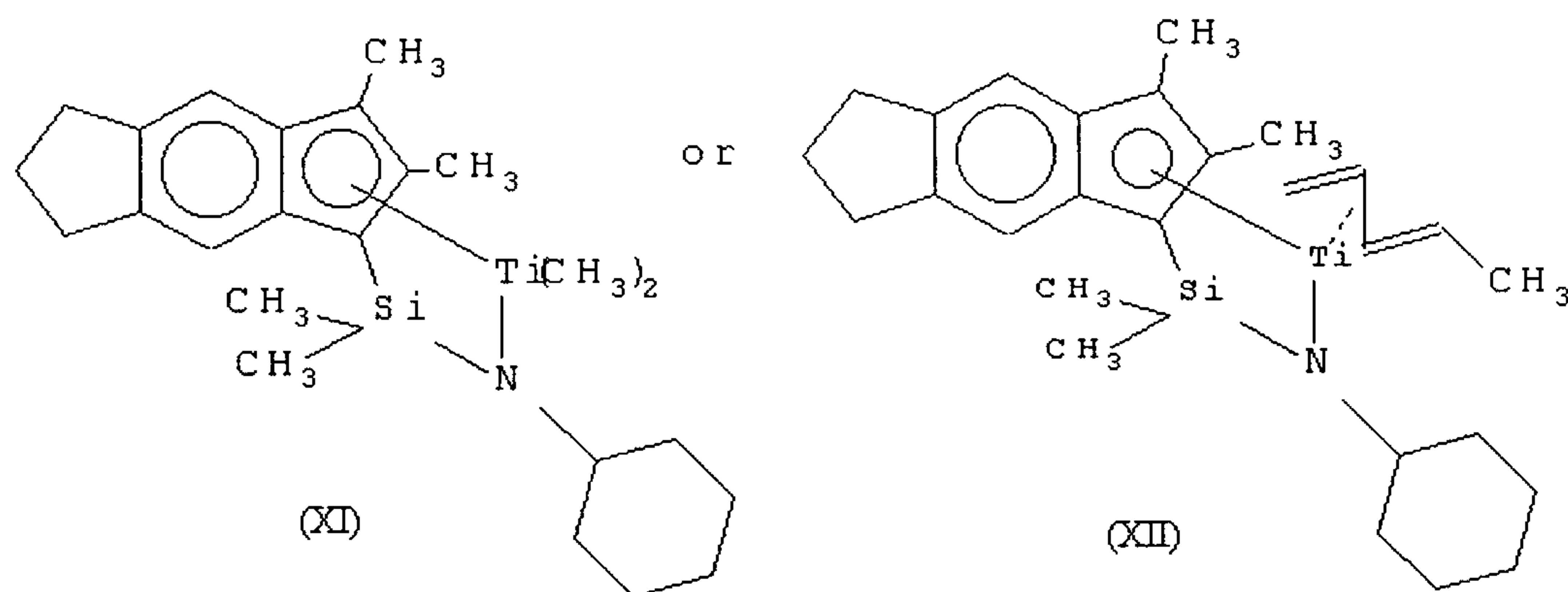
when p and r were 0, q was 1, M was in the +2 formal oxidation state, and X' was 1,4-diphenyl-1,3-butadiene or 1,3-pentadiene.

5 Especially preferred coordination complexes corresponding to the previous formulas (XIV) and (XV) were uniquely substituted depending on the particular end use thereof. In particular, highly useful metal complexes for use in catalyst compositions for the copolymerization of ethylene, one or more monovinyl aromatic monomers, and optionally an α -olefin or diolefin comprise the foregoing complexes (XIV) or (XV)
 10 wherein R' was C₆₋₂₀ aryl, especially phenyl, biphenyl or naphthyl, and R'' was hydrogen or methyl, especially hydrogen. More preferably such complexes were 3-phenyl-substituted s-indecenyl complexes corresponding to formulae (IX) or (X):

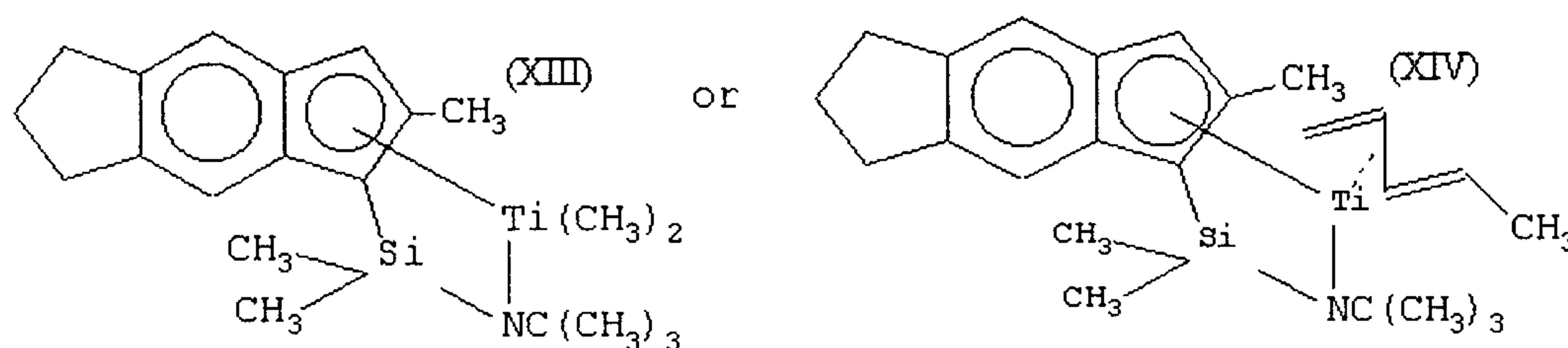


Highly useful metal complexes for use in the second component of the dual CGC
 15 catalyst system comprise the foregoing complexes (XIV) or (XV) wherein R' was C₁₋₄ alkyl, N,N-dimethylamino or 1-pyrrolidinyl, and R'' was hydrogen or C₁₋₄ alkyl. Moreover, in such complexes, Y was preferably a cyclohexylamido group, X was methyl, p was two, and both q and r is 0. Most preferably such complexes were 2,3-dimethyl-substituted s-indecenyl complexes corresponding to formula (XI) or (XII):

20



Finally, highly useful metal complexes for use in the second component of the dual CGC catalyst system for the copolymerization of ethylene, an α -olefin and a diene, especially ethylene, propylene and a nonconjugated diene, such as ethyldenenorbornene or 1,4-hexadiene, comprise the foregoing complexes (XIV) or (XV) wherein R' was hydrogen, and R'' was C₁₋₄ alkyl, especially methyl. Most preferred were 2-methyl-substituted s-indecenyl complexes corresponding to formula (XIII) or (XIV):



10

Illustrative metal complexes that may be employed in the preparation of the second component of the dual CGC systems of the present invention were further described in WO 98/27103.

The metal complexes used in the practice of this invention were prepared by well-known synthetic techniques. One preferred process for preparing the metal complexes was disclosed in USP 5,491,246. The reactions were conducted in a suitable noninterfering solvent at a temperature from -100 to 300 C, preferably from -78 to 100 C, most preferably from 0 to 50 C. A reducing agent may be used to cause M to be reduced from a higher to a lower oxidation state. Examples of suitable reducing agents were alkali metals, alkaline earth metals, aluminum and zinc, alloys of alkali metals or alkaline earth metals such as sodium/mercury amalgam and sodium/potassium alloy, sodium

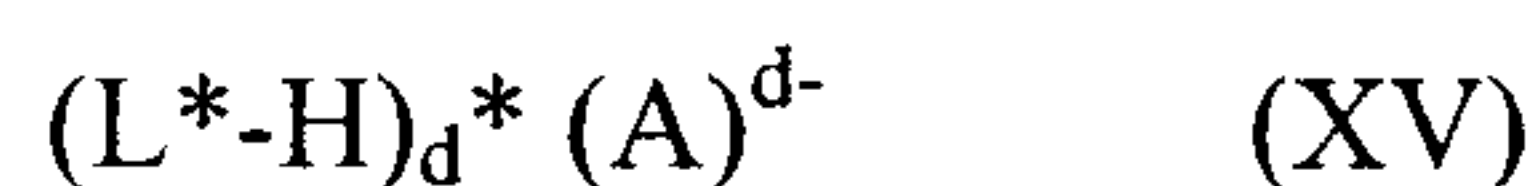
naphthalenide, potassium graphite, lithium alkyls, lithium or potassium alkadienyls, and Grignard reagents.

Suitable reaction media for the formation of the complexes include aliphatic and aromatic hydrocarbons, ethers, and cyclic ethers, particularly branched chain
5 hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; aromatic and hydrocarbyl substituted aromatic compounds such as benzene, toluene, and xylene, C₁₋₄ dialkyl ethers, C₁₋₄ dialkyl ether derivatives of (poly)alkylene glycols, and tetrahydrofuran. Mixtures of
10 the foregoing were also suitable.

Suitable activating cocatalysts useful in combination with the A) metal complexes were those compounds capable of abstraction of an X substituent from A) to form an inert, noninterfering counter ion, or that form a zwitterionic derivative of A). Suitable activating cocatalysts for use herein include perfluorinated tri(aryl)boron compounds, and
15 most especially tris(pentafluorophenyl)borane; nonpolymeric, compatible, noncoordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium, phosphonium, oxonium, carbonium, silylium or sulfonium salts of compatible, noncoordinating anions, and ferritenium salts of compatible, noncoordinating anions. Suitable activating techniques
20 include the use of bulk electrolysis (explained subsequently in more detail). A combination of the foregoing activating cocatalysts and techniques may be employed as well. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes in the following references: EP-A-277,003, USP 5,153,157, USP 5,064,802, EP-A-468,651, USP 5,721,185, USP
25 5,350,723. More particularly, suitable ion-forming compounds useful as cocatalysts in one embodiment of the present invention comprise a cation which was a Bronsted acid capable of donating a proton, and a compatible, noncoordinating anion, A⁻.

Preferred anions were those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion was capable of balancing the charge
30 of the active catalyst species (the metal cation) which may be formed when the two components were combined. Also, the anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitrites. Suitable metals include, but were not limited to,

aluminum, gold and platinum. Suitable metalloids include, but were not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom were, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, were available commercially. Preferably such cocatalysts may be represented by general formula (XV):



wherein:

10 L^* was a neutral Lewis base;

$(L^*-H)^+$ was a Bronsted acid;

A^{d-} is a noncoordinating, compatible anion having a charge of $d-$, and

d was an integer from 1-3.

More preferably A^{d-} corresponds to formula (XVI):

15



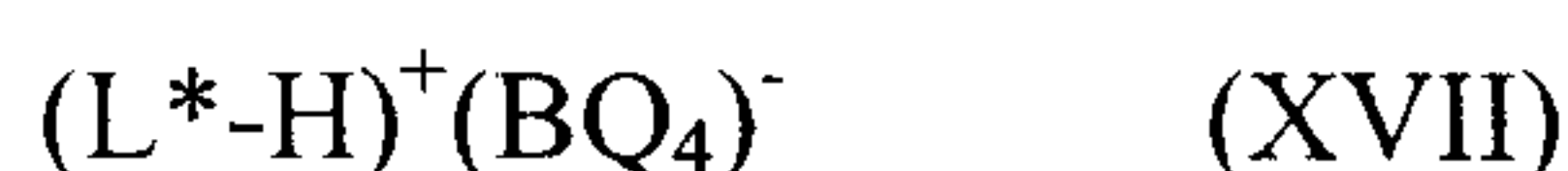
wherein:

M' was boron or aluminum in the formal +3 formal oxidation state; and

20 Q independently each occurrence was selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted hydrocarbyl, halosubstituted hydrocarbyloxy, and

halosubstituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence was Q halide. Examples of suitable hydrocarbyloxy Q groups were disclosed in USP 5,296,433.

30 In a more preferred embodiment, d was 1, that is, the counter ion has a single negative charge and was A^- . Activating cocatalysts comprising boron which were particularly useful in the preparation of the first catalyst component of this invention may be represented by general formula (XVII):



wherein:

L* was as previously defined;

B was boron in a formal oxidation state of 3; and

Q was a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion was Q hydrocarbyl.

Most preferably, Q was each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention were trisubstituted ammonium salts such as: trimethylammonium tetrakis(pentafluorophenyl) borate, triethylammonium tetrakis(pentafluorophenyl) borate, tripropylammonium tetrakis(pentafluorophenyl) borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate, tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate, N,N-dimethylanilinium benzyltris(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(4-(t-butyl)dimethylsilyl)-2,3,5,6-tetrafluorophenyl) borate, N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2,3,5,6-tetrafluorophenyl) borate, N,N-di(n-hexadecanyl)-N-methylammonium tetrakis (2,3,4,5,6-pentafluorophenyl) borate, N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate, N,N-diethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate, trimethylammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, triethylammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, tripropylammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, tri(n-butyl)ammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, dimethyl(t-butyl)ammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, N,N-dimethylanilinium tetrakis (2,3,4,6-tetrafluorophenyl) borate, N,N-diethylanilinium tetrakis (2,3,4,6-tetrafluorophenyl) borate, and N,N-dimethyl-2,4,6-trimethylanilinium tetrakis (2,3,4,6-tetrafluorophenyl) borate; disubstituted ammonium salts such as: di-(i-propyl) ammonium tetrakis(pentafluorophenyl) borate, and dicyclohexylammonium tetrakis(pentafluorophenyl) borate; trisubstituted phosphonium salts such as: triphenylphosphonium tetrakis(pentafluorophenyl) borate, tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate; disubstituted oxonium salts such as: diphenyloxonium

tetrakis(pentafluorophenyl) borate, di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and di(2,6-dimethylphenyl) oxonium tetrakis(pentafluorophenyl) borate; disubstituted sulfonium salts such as: diphenylsulfonium tetrakis(pentafluorophenyl) borate, di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and bis(2,6-dimethylphenyl)sulfonium tetrakis(pentafluorophenyl) borate.

Preferred $(L^*-H)^+$ cations were N,N-dimethylanilinium, tributylammonium and N,N-di(n-hexadecanyl)-N-methylammonium.

Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by formula (XVIII):



wherein:

Ox^{e+} was a cationic oxidizing agent having a charge of $e+$;

e was an integer from 1 to 3; and

A^{d-} and d were as previously defined.

Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+ or Pb^{+2} . Preferred embodiments of A^{d-} were those anions previously defined with respect to the Bronsted acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl) borate.

Another suitable ion forming, activating cocatalyst comprises a compound which was a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula (XIX):



wherein:

$\odot^+$ was a C_{1-20} carbenium ion; and

A^- was as previously defined. A preferred carbenium ion was the trityl cation, that is triphenylmethylium.

A further suitable ion forming, activating cocatalyst comprises a compound which was a salt of a silylium ion and a noncoordinating, compatible anion represented by formula (XX):



wherein:

R^v was C_{1-10} hydrocarbyl, and A^- was as previously defined.

Preferred silylium salt activating cocatalysts were trimethylsilylium
5 tetrakis(pentafluorophenyl) borate, triethylsilylium tetrakis(pentafluorophenyl) borate and
ether substituted adducts thereof. Silylium salts have been previously generically
disclosed in J. Chem Soc. Chem. Comm., 1993, 383-384, as well as Lambert, J.B., et al,
Organometallics, 1994, 13, 2430-2443. The use of the above silylium salts as activating
cocatalysts for addition polymerization catalysts as claimed in USP 5,625,087.

10 Certain complexes of alcohols, mercaptans, silanols, and oximes with
tris(pentafluorophenyl)borane were also effective catalyst activators and may be used
according to the present invention. Such cocatalysts were disclosed in USP 5,296,433.

The technique of bulk electrolysis involves the electrochemical oxidation of the
metal complex under electrolysis conditions in the presence of a supporting electrolyte
15 comprising a noncoordinating, inert anion. In the technique, solvents, supporting
electrolytes and electrolytic potentials for the electrolysis were used such that electrolysis
byproducts that would render the metal complex catalytically inactive were not
substantially formed during the reaction. More particularly, suitable solvents were
materials that were (i) liquids under the conditions of the electrolysis (generally
20 temperatures from 0 to 100 C), (ii) capable of dissolving the supporting electrolyte, and
(iii) inert. "Inert solvents" were those that were not reduced or oxidized under the
reaction conditions employed for the electrolysis. It was generally possible in view of the
desired electrolysis reaction to choose a solvent and a supporting electrolyte that were
unaffected by the electrical potential used for the desired electrolysis. Preferred solvents
25 include difluorobenzene (all isomers), dimethoxyethane (DME), and mixtures thereof.

The electrolysis may be conducted in a standard electrolytic cell containing an
anode and cathode (also referred to as the working electrode and counterelectrode
respectively). Suitable materials of construction for the cell were glass, plastic, ceramic
and glass-coated metal. The electrodes were prepared from inert conductive materials, by
30 which were meant conductive materials that were unaffected by the reaction mixture or
reaction conditions. Platinum or palladium were preferred inert conductive materials.
Normally an ion permeable membrane such as a fine glass grit separates the cell into
separate compartments, the working electrode compartment and counterelectrode

compartment. The working electrode was immersed in a reaction medium comprising the metal complex to be activated, solvent, supporting electrolyte, and any other materials desired for moderating the electrolysis or stabilizing the resulting complex. The counterelectrode was immersed in a mixture of the solvent and supporting electrolyte.

5 The desired voltage may be determined by theoretical calculations or experimentally by sweeping the cell using a reference electrode such as silver electrode immersed in the cell electrolyte. The background cell current, the current draw in the absence of the desired electrolysis, was also determined. The electrolysis was completed when the current drops from the desired level to the background level. In this manner, complete conversion of

10 the initial metal complex can be easily detected.

Suitable supporting electrolytes were salts comprising a cation and a compatible, noncoordinating anion, A^- . Preferred supporting electrolytes were salts corresponding to the formula G^+A^- wherein G^+ was a cation which was nonreactive towards the starting and resulting complex, and A^- was as previously defined.

15 Examples of cations, G^+ , include tetrahydrocarbyl substituted ammonium or phosphonium cations having up to 40 nonhydrogen atoms. Preferred cations were the tetra(n-butylammonium)- and tetraethylammonium- cations

During activation of the complexes of the present invention by bulk electrolysis the cation of the supporting electrolyte passes to the counterelectrode and A^- migrates to

20 the working electrode to become the anion of the resulting oxidized product. Either the solvent or the cation of the supporting electrolyte was reduced at the counterelectrode in equal molar quantity with the amount of oxidized metal complex formed at the working electrode. Preferred supporting electrolytes were tetrahydrocarbylammonium salts of tetrakis(perfluoroaryl) borates having from 1 to 10 carbons in each hydrocarbyl or

25 perfluoroaryl group, especially tetra(n-butylammonium)tetrakis(pentafluorophenyl) borate.

A further recently discovered electrochemical technique for generation of activating cocatalysts was the electrolysis of a disilane compound in the presence of a source of a noncoordinating compatible anion. All of the foregoing techniques were more

30 fully disclosed and claimed in USP 5,372,682. In as much as the activation technique ultimately produces a cationic metal complex, the amount of such resulting complex formed during the process can be readily determined by measuring the quantity of energy used to form the activated complex in the process.

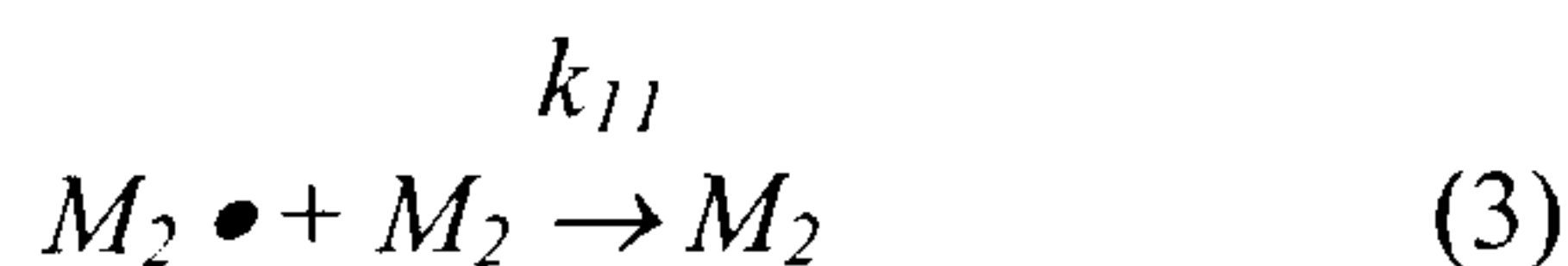
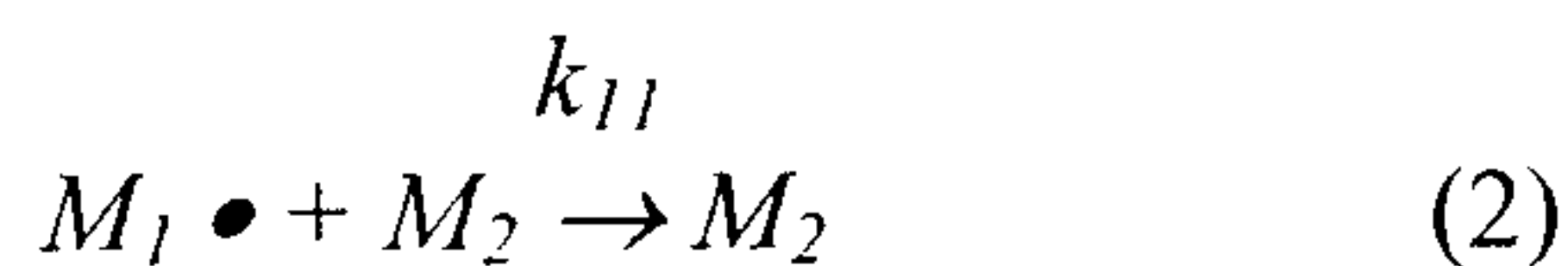
Alumoxanes, especially methylalumoxane or triisobutylaluminum modified methylalumoxane were also suitable activators and may be used for activating the present metal complexes.

Preferred activating cocatalysts include trispentafluorophenylborane and
5 di(hydrogenated-tallowalkyl)methylammonium tetrakis-(pentafluorophenyl) borate.

The molar ratio of metal complex:activating cocatalyst employed preferably ranges from 1:1000 to 2:1, more preferably from 1:5 to 1.5:1, most preferably from 1:2 to 1:1.

The amount of first CGC to second CGC in the mixed catalyst system can vary
10 widely and to convenience. Typically, the minimum ratio, in weight percent based on the combined weight of the metals, of first CGC to second CGC was 1:99, preferably 5:95 and most preferably 75:25. The typical maximum ratio, again in weight percent based on the combined weight of the metals, was 99:1, preferably 95:5 and most preferably 25:75.

The reactivity ratios describe the copolymerization of the monomers M_1 and M_2 as
15 shown in the following equations where M_1 was ethylene and M_2 was a higher α -olefin. The value of r_1 was used to describe the reactivity of a catalyst to comonomers with a lower value of r_1 indicating greater reactivity for comonomer incorporation.



$$r_1 = k_{11} / k_{12} \quad (5)$$

$$r_2 = k_{22} / k_{21} \quad (6)$$

30

The comonomer concentration in the polymer and reactor were then related by:

$$35 \quad \frac{dM_1}{dM_2} = \frac{M_1 r_1}{M_2 r_2} \frac{M_1 + M_2}{M_2 + M_1} \approx \frac{m_1}{m_2} \quad (7)$$

where M1 and M2 refer to the reactor concentrations, and m1 and m2 refer to the polymer composition.

The reactivity ratios can be obtained using the Fineman-Ross method in which the monomer concentrations in the reactor and in the final polymer were related at low conversions by solving equation (7) graphically and obtaining r_1 as the slope and the intercept being minus r_2 .

$$\frac{M_1}{M_2} - \frac{\left[\frac{M_1}{M_2} \frac{m_2}{m_1} \right]}{\left[\frac{M_1}{M_2} \frac{m_2}{m_1} \right]} = r_1 \left[\frac{M_1}{M_2} \right]^2 \left[\frac{m_2}{m_1} \right] - r_2 \quad (8)$$

The lower the value of r_1 , the closer were the monomer and comonomer in reactivity, and the greater the incorporation rate of the comonomer. When two catalysts that differ in the value of r_1 were used together in a single reaction vessel to promote the same ethylene/ α -olefin polymerization, a polymer blend will be produced, that is, a product comprising two polymer components differing in molecular architecture. The polymer component produced through the action of the catalyst with the lower reactivity ratio will contain more comonomer than the polymer component produced through the action of the catalyst with the higher reactivity ratio. For purposes of describing this invention, catalysts with reactivity ratios that differ by more than 50 percent from one another with respect to the polymerization of ethylene and a given α -olefin at the same temperature will produce a polymer blend in which the blend components do not have a substantially uniform molecular architecture, and catalysts with reactivity ratios that differ by 50 percent or less, preferably 30 percent or less, from one another with respect to the polymerization of ethylene and a given α -olefin at the same temperature will produce a polymer blend in which the blend components do have a substantially uniform molecular architecture. For interpolymer blends derived from three or more comonomers, particularly those interpolymer blends in which one of the comonomers was a polyene, the molecular architecture of the blend components may not be substantially uniform even though the reactivity ratios of the catalysts differ by less than 50 percent with respect to ethylene and the α -olefin because the reactivity ratios of the catalysts may differ by more than 50 percent with respect to ethylene and the second comonomer.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0-250 C, preferably 30 to 200 C and pressures from atmospheric to

10,000 atmospheres. Suspension, solution, slurry, gas phase, solid state powder polymerization or other process conditions may be employed if desired. A support, especially silica, alumina, or a polymer (especially poly(tetrafluoroethylene) or a polyolefin) may be employed, and desirably was employed when the catalysts were used
5 in a gas phase polymerization process. The support was preferably employed in an amount to provide a weight ratio of catalyst (based on metal):support from 1:100,000 to 1:10, more preferably from 1:50,000 to 1:20, and most preferably from 1:10,000 to 1:30.

In most polymerization reactions the molar ratio of catalyst:polymerizable compounds employed was from 10^{-12} :1 to 10^{-1} :1, more preferably from 10^{-9} :1 to 10^{-5} :1.
10 In this ratio, "catalyst" means the mixed catalyst system. Suitable solvents for solution polymerization were inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated
15 hydrocarbons such as perfluorinated C_{4-10} alkanes, and alkyl-substituted aromatic compounds such as benzene, toluene, xylene, and ethylbenzene. Suitable solvents also include liquid olefins that may act as monomers or comonomers.

Utilizing the mixed catalyst system of the present invention, α -olefin homopolymers and copolymers having densities from 0.85 g/cm^3 to 0.97 g/cm^3 , and
20 Mooney viscosities of from less than 0.01 to 150 were readily attained in a highly efficient process.

The mixed catalyst systems of the present invention were particularly advantageous for the production of ethylene homopolymers and ethylene/ α -olefin copolymers having long chain branching, often high levels of long chain branching. The
25 use of this system in continuous polymerization processes, especially continuous, solution polymerization processes, allows for elevated reactor temperatures which favor the formation of vinyl terminated polymer chains that may be incorporated into a growing polymer, thereby giving a long chain branch. Although relatively large amounts of α -olefin disfavor the formation of long chain branches, the polymerization conditions can be
30 adjusted as taught in WO 1998/049212 to offset, at least partially, this tendency. The use of the present catalyst compositions advantageously allows for the economical production

of ethylene/ α -olefin copolymers having processability similar to high pressure, free radical produced low-density polyethylene.

The mixed catalyst systems used in this invention may also be advantageously employed to prepare olefin polymers having improved processing properties by polymerizing ethylene alone or ethylene/ α -olefin mixtures with low levels of a "H" branch inducing diene, such as norbornadiene, 1,7-octadiene, or 1,9-decadiene. The unique combination of elevated reactor temperatures, high molecular weight (or low melt indices) at high reactor temperatures and high comonomer reactivity advantageously allows for the economical production of polymers having excellent physical properties and processability. Preferably such polymers comprise ethylene, a C_{3-20} α -olefin and a "H"-branching comonomer. Preferably, such polymers were produced in a solution process, most preferably a continuous solution process.

The individual catalyst components of the mixed catalyst system may be prepared as a homogeneous catalyst by addition of the requisite components to a solvent in which polymerization will be carried out by solution polymerization procedures. These catalyst components may also be prepared and employed as a heterogeneous catalysts by adsorbing the requisite components on an inert inorganic or organic particulated solid. Examples of such solids include, silica, silica gel, alumina, trialkylaluminum compounds, and organic or inorganic polymeric materials, especially polyolefins. In an preferred embodiment, a heterogeneous catalyst was prepared by coprecipitating the metal complex, an inert, inorganic compound and an activator, especially an ammonium salt of a hydroxyaryl(trispentafluorophenyl)borate, such as an ammonium salt of (4-hydroxy-3,5-ditertiarybutylphenyl)(trispentafluorophenyl)borate. A preferred inert, inorganic compound for use in this embodiment was a tri (C_{1-4} alkyl) aluminum compound.

When prepared in heterogeneous or supported form, the catalyst compositions were employed in a slurry or gas phase polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product was substantially insoluble. Preferably, the diluent for slurry polymerization was one or more hydrocarbons with less than 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise the α -olefin monomer or a mixture of different α -olefin monomers may be used in whole or part

as the diluent. Most preferably at least a major part of the diluent comprises the α -olefin monomer or monomers to be polymerized.

At all times, the individual ingredients as well as the recovered catalyst components must be protected from oxygen and moisture. Therefore, the catalyst components and catalysts must be prepared and recovered in an oxygen and moisture free atmosphere. Preferably, therefore, the reactions were performed in the presence of an dry, inert gas such as, for example, nitrogen.

The polymerization may be carried out as a batchwise or a continuous polymerization process. A continuous process was preferred, in which event the mixed catalyst system, ethylene, comonomer, and optionally solvent were continuously supplied to the reaction zone and from which polymer product was continuously removed.

Without limiting in any way the scope of the invention, one means for carrying out such a polymerization process was as follows: In a stirred-tank reactor, the monomers to be polymerized were introduced continuously together with solvent and an optional chain transfer agent. The reactor contains a liquid phase composed substantially of monomers together with any solvent or additional diluent and dissolved polymer. If desired, a small amount of a "H"-branch inducing diene such as norbornadiene, 1,7-octadiene or 1,9-decadiene may also be added. The metal complexes and cocatalysts of the mixed catalyst system were continuously introduced into the reactor liquid phase.

The reactor temperature and pressure were controlled by adjusting the solvent/monomer ratio, the catalyst addition rate, as well as by cooling or heating coils, jackets or both. The polymerization rate was controlled by the rate of catalyst addition. The ethylene content of the polymer product was determined by the ratio of ethylene to comonomer in the reactor, which was controlled by manipulating the respective feed rates of these components to the reactor. The polymer product molecular weight was controlled, optionally, by controlling other polymerization variables such as the temperature, monomer concentration, or by the previously mention chain transfer agent, such as a stream of hydrogen introduced to the reactor, as was well known in the art.

The reactor effluent was contacted with a catalyst kill agent such as water or alcohol. The polymer solution was optionally heated, and the polymer product was recovered by flashing off gaseous monomers as well as residual solvent or diluent at reduced pressure, and, if necessary, conducting further devolatilization in equipment such as a devolatilizing extruder. In a continuous process the mean residence time of the

catalyst and polymer in the reactor generally was from 5 minutes to 8 hours, and preferably from 10 minutes to 6 hours. By using a mixed catalyst system that incorporates large amounts of hindered monovinyl monomer, hindered monovinyl homopolymer formed from residual quantities of the monomer were substantially reduced.

5 In one embodiment of this invention, the single reaction vessel in which the polymer blend was prepared was one reactor of a multiplicity of reactors deployed either in parallel or in series. In such deployments, the polymer blend of the single reaction vessel can be a feed to a subsequent reactor (series deployment), or it can be blended with the output from another reactor (parallel deployment).

10 The polymer blends of this invention have a wide range of uses. The blends were useful in the manufacture of molded articles such as toys, toy parts, sporting goods, medical goods, soft touch parts of a relatively low shore A hardness, and automotive parts, and extruded goods such as tubing and profiles. Other applications for these blends include wire and cable, footwear, building and construction materials, adhesives, films
15 and fibers, flooring, foams, weather stripping, oil modification, general rubber goods, extruded sheets, instrument panel skins, food packaging, electronic components and the like. These blends can be crosslinked by any of the various crosslinking agents, for example, peroxide, sulfur, phenolics, azides and radiation, and/or grafted using maleic anhydride, silane or one or more of the other reactive monomers which can modify the
20 functional performance of the blend. These blends can also be mixed with other materials such as thermoplastic olefins, elastomers and vulcanizates for use in various extrusion, injection molding, calendering, rotomolding, slush molding, blow molding, thermoforming and compression molding applications.

25 Examples

 The skilled artisan will appreciate that the present invention disclosed may be practiced in the absence of any component which has not been specifically disclosed. The following examples were provided as further illustration of the invention and were not to be construed as limiting. Unless stated to the contrary all parts and percentages were
30 expressed on a weight basis.

Batch Reactor Run Description

Additive solution: The additive solution was prepared by dissolving PEPQ (an antioxidant from Sandoz) and Irganox 1076 (a hindered phenolic antioxidant from Ciba-Geigy) in 500 ml of toluene. The concentration of the solution was 20 mg of total additive per 1 ml of solution.

Polymerization: A typical run using a mixed catalyst system was described. A one-gallon stirred reactor was charged with Isopar E (mixed alkanes; available from Exxon Chemicals Inc.), octene-1, hydrogen and, if desired, 5-ethylidene-2-norbornene (ENB). If ENB was added, then it was added to the reactor prior to the addition of hydrogen. All liquid components were measured by mass flow. The reactor was heated to the desired temperature and saturated with ethylene.

The catalyst was prepared in a drybox by syringing together the appropriate components with additional solvent to give a total volume of 18 ml. In mixed catalyst runs, the two components were added in molar ratio of metal (1 to 1 unless stated otherwise in the Tables). The catalyst solution was then transferred by syringe to a catalyst addition loop and injected into the reactor over approximately 4 minutes using a flow of high-pressure solvent. An exotherm of 10 C was observed. The polymerization was allowed to proceed for 10 minutes while feeding ethylene on demand to maintain a relatively constant pressure (typically between 450 and 465 psi. The maximum flow of ethylene was typically 20 g/min. The amount of ethylene consumed during the reaction was monitored using a mass flowmeter.

The polymer solution was then dumped from the reactor into a nitrogen-purged glass kettle. An aliquot of the additive solution described above was added to this kettle and the solution stirred thoroughly (the amount of additive used was chosen based on the total ethylene consumed during the polymerization to produce 1000 ppm of each additive in the polymer). The polymer solution was dumped into a tray, air dried overnight, then thoroughly dried in a vacuum oven for one day. Some of the polymers and polymer blends were then measured according to ASTM tests for tensile @ break, elongation @ break, I_2 and I_{10} .

Table 1A reports the batch reactor preparation of ethylene/1-octene polymer blends and polymers using two mixed catalyst systems (A/B in Runs 1-6, and B/C in Runs 7-9) and the individual catalyst components of the systems, respectively, along with selected physical characteristics of the polymers and polymer blends. Runs 4-6 were

conducted at a temperature of 20 C greater than Runs 1-3. Runs 3 and 6 were representative of the process and polymer blends of this invention. Run 9 reports a comparative process and polymer blend. Tables 1B, 1C and 1D report similar information for ethylene/propylene/ENB, ethylene/butene/ENB and ethylene/butene polymer blends and polymers.

TABLE 1A

**Batch Reactor Operational Data and Polymer Blend Properties
of Ethylene/1-Octene Polymers and Polymer Blends**

Run Number	1	2	3	4	5	6
Catalyst*	A	A/B	B	A	A/B	B
Temp, C	89.5	89.4	89.9	109.9	109.8	109.9
1-Octene, g	351.4	351.1	350.9	450.2	451.2	450.1
Ti, μ mole	1.50	1.25	1.25	1.75	1.75	1.50
B/Ti	4.00	3.96	3.96	4.03	4.03	4.00
Al/Ti	5.00	5.20	5.20	5.14	5.14	5.00
Exotherm C	8.7	9.2	6.0	4.1	8.2	5.3
C ₂ Flow, max	20.1	19.7	15.8	21.3	25.0	20.6
C ₂ rate end	0	0.4	0	0	0	0
C ₂ used, g	54.8	59.4	52.1	43.3	62.8	50.5
Calculated Efficiency	763,105	992,506	870,864	516,887	749,018	703,031
Solvent, g	1504.3	1505.4	1500.2	1402.7	1402.3	1405.0
Pressure, psig	457.4	456.8	458.1	456.3	456.6	456.1
C ₂ load, g	212.0	214.6	212.6	181.0	182.5	182.2
C ₂ pressure, psig	444.3	443.8	445.6	437.7	439.7	439.2
H ₂ mmole	8.0	8.0	8.0	8.1	8.2	8.2
Mw	72,400	130,700	198,800	49,500	87,000	125,200
Mn	39,100	54,600	102,500	25,800	35,800	63,000
MWD	1.85	2.39	1.94	1.92	2.43	1.99
Mw1	-	222,827	-	-	150,081	-
Mw2	-	74,454	-	-	51,747	-
MW Ratio Hi/Lo	-	2.99	-	-	2.90	-
I ₂	6.27	0.796	0.16	30.99	4.35	0.99
I ₁₀	38.62	6.00	0.93	188.02	33.35	6.41
I ₁₀ /I ₂	6.2	7.5	5.8	6.1	7.7	6.5
DSC Tm Peak Melting	67.69	62.87	59.91	65.42	59.65	50.95
% Crystallized	23.09	19.85	17.89	21.07	19.58	15.06
DSC Tg	-51.69	-54.99	-51.35	-52.56	-53.47	-58.13
Tc (onset)	53.03	50.35	48.58	53.19	48.31	40.37
Tc (peak)	50.09	47.89	45.95	47.24	44.13	36.18
J/g	70.05	61.26	53.02	54.55	54.49	48.64

*A - (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium 1,3-pentadiene.

B - (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silane titanium 1,3-pentadiene.

TABLE 1A (Cont'd)

**Batch Reactor Operational Data and Polymer Blend Properties
of Ethylene/1-Octene Polymers and Polymer Blends**

Run Number-	7	8	9 (Comp)
Catalyst*	B	C	C/B
Temp, C	109.9	110.1	109.6
Octene, g	750.7	750.9	750.6
Ti, μ mole	1.50	1.50	1.40
B/Ti	4.00	4.00	3.96
Al/Ti	5.00	5.00	5.00
Exotherm C	3.5	3.9	1.9
C ₂ Flow, max	17.1	22.3	10.2
C ₂ rate end	0	0.1	0.2
C ₂ used, g	38.7	28.3	13.1
Calculated Efficiency	538,701	393,199	196,149
Solvent, g	1078.2	1081.2	1081.5
Pressure, psig	456.1	455.5	456.3
C ₂ load, g	185.7	184.9	186.6
C ₂ press	443.4	442.1	443.4
H ₂ mmole	1.6	1.6	1.6
Mw	142,400	324,700	253,600
Mn	74,100	182,000	104,000
MWD	1.92	1.78	2.44
Mw1	-	-	359,791
Mw2	-	-	124,571
MW Ratio Hi/Lo	-	-	2.89
DSC Peak Melting	Broad	66.51	78.38
% Crystallized	10.23	23.20	20.19
DSC Tg	-59.77	-46.05	-61.49
Tc (onset) #1	10.10	66.51	68.39
Peak Cooling #1	0.31	63.94	65.79
J/G #1	30.54	67.74	54.56
Tc (onset) #2	-	-	-
Peak Cooling #2	-	-	-0.89

5 * B - (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silanetitanium 1,3-pentadiene.

C [N-(1,1-dimethylethyl)-1,1-dimethyl-1-((1,2,3,3a,7a-h)-3-(1-pyrrolidinyl)-1H-inden-1-yl)silanaminato-(2-)-N] [(2,3,4,5,-h)-2,4-pentadiene)]-titanium.

As the data of Runs 1-6 shows, polymer blends made with a mixed catalyst system have a larger MWD than the polymers made under similar polymerization conditions with only one of the mixed catalyst components (compare Runs 1 and 2 with 3; and Runs 4 and 5 with 6). Moreover, the polymer blends of Runs 3 and 6 have a substantially uniform molecular architecture as demonstrated by a single DSC T_m melting peak. In contrast, although Runs 7-9 also report that the blend has a larger MWD than the polymers made under similar polymerization conditions with only one of the mixed catalyst components (compare Runs 7 and 8 with 9), the components of the blend do not have a substantially uniform molecular architecture as demonstrated by the presence of two DSC peaks (note Peak Cooling #2). These results were consistent with the similarity in reactivity ratios of Catalysts A and B, and the dissimilarity in reactivity ratios between Catalysts B and C, with respect to ethylene and 1-octene, all as reported in Table 7A.

Also of interest was the fact that the high Mw/low Mw ratio was relatively constant over Runs 3, 6 and 9 despite a 20 C temperature difference and the use of catalysts, that is, A and B vs. C, of different reactivity ratios (as reported in Table 7A). In addition, the I₁₀/I₂ (rheology ratio) of the polymer blends made by the mixed catalyst system shows higher shear sensitivity which equates to improved processability in injection molded, extrusion or blow molded applications.

TABLE 1B

**Batch Reactor Operational Data and Physical Properties
of Ethylene/Propylene/ENB Polymers and Polymer Blends**

Run Number	Percent Catalyst A*	Percent Catalyst B*	Propylene mass, g	ENB mass, g	Temp, C	H ₂ mmol	Ethylene mass, g	Ethylene partial pressure, psig
10	100%	0%	200.8	40.2	99.8	12.50	143.7	318.3
11	75%	25%	200	40.3	99.9	12.10	148.6	321.4
12	50%	50%	202	40.1	100.3	12.00	149.5	328.8
13	25%	75%	201.2	40.3	99.7	12.2	149.6	329.7
14	0%	100%	201.1	40.2	100.4	12.3	150.3	335

Run Number	Percent Catalyst A	Efficiency MM lb PE/ lb Ti	Ti μ mole	B/ Ti Ratio	Al/ Ti Ratio	Exotherm, C	Max. Temp, C	Solvent mass, g	Total Press, psig
10	100	1.36	1	3	10	3.3	103.1	1401.3	461.50
11	75	1.82	1	3	10	3.7	103.6	1403.8	458.50
12	50	1.71	1.5	3	10	9.3	109.6	1403.1	463.90
13	25	1.67	1.25	3	10	3.4	103.1	1406.3	462.4
14	0	1.15	1.5	3	10	2.2	102.6	1405.1	462.2

Run Number	GPC Mw	GPC Mn	GPC MWD	Mw1	Mw2	Hi/Lo Mw Ratio	Tc (onset) C	Tc (peak) C	Tg C	Tm C
10	174700	87700	1.99	-	52353	-	10.98	5.73	-40.42	3.77
11	165500	63700	2.6	174700	51165	4.15	12.73	7.21	-41.58	9.01
12	123800	41700	2.97	217056	51423	3.96	14.95	9.17	-41.68	7.3
13	93900	33100	2.84	202696	56900	3.73	18.87	12.04	-41.52	10.41
14	56900	30200	1.88	191659	-	-	21.62	13.59	-42.94	6.73

Run Number	FTIR [†] Method	FTIR [†] Percent Ethylene	FTIR [†] Percent Propylene	FTIR [†] Percent ENB	Ethylene/propylene ratio	Density	%Xtal
10	EPDM	67.1	26.2	6.7	71.9/28.1	0.867	10.47
11	EPDM	66.4	27.8	5.8	70.5/29.5	0.865	10.78
12	EPDM	66.4	28.6	5.0	69.9/30.1	0.865	11.71
13	EPDM	66.9	28.3	4.8	70.3/29.7	0.866	13.51
14	EPDM	66.0	30.2	3.9	68.6/31.4	0.863	13.83

TABLE 1B

**Batch Reactor Operational Data and Physical Properties
of Ethylene/Propylene/ENB Polymers and Polymer Blends**

Run Number	Percent Catalyst A	Tensile @ Break (psi)	Elongation @ Break (%)	I ₂ @ 190C/2.16 kg	I ₁₀ @ 190C/10.1 kg	I ₁₀ /I ₂ @ 190C
10	100	381	1988	0.20	1.23	6.26
11	75	445	1699	0.23	1.50	6.51
12	50	403	1904	0.80	6.64	8.28
13	25	438	1999	2.42	21.52	8.88
14	0	102	306	17.14	102.48	5.98

*A - (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silanetitanium 1,3-pentadiene.

B - (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silanetitanium 1,3-pentadiene.

5 [±] Fourier Transformation Infrared Spectroscopy.

TABLE 1C

**Batch Reactor Operational Data and Physical Properties
of Ethylene/Butene/ENB Polymer and Polymer Blends**

Run Number	Percent Catalyst A*	Percent Catalyst B*	Butene mass, g	ENB mass, g	Temp, C	H ₂ mmol	Ethylene mass, g	Ethylene partial pressure psig
15	100%	0%	265.5	40.0	100	12.2	185.6	399.7
16	75%	25%	265.2	40.5	100.1	12.2	183	395.3
17	50%	50%	265.4	40.4	99.4	12	183.6	392.9
18	25%	75%	265.5	40.4	99.7	12.1	182	391.3
19	0%	100%	265	40.2	100.3	12.2	182.4	399.4

Run Number	Percent Catalyst A	Efficiency MM lb PE/ lb Ti	Ti μ mole	B/ Ti Ratio	Al/ Ti Ratio	Exotherm, C	Max. Temp, C	Solvent mass, g	Total Press, psig
15	100%	1.94	1	3	10	4.7	104.7	1401	463.5
16	75%	2.96	0.75	3	10	5.7	105.8	1401.1	463.7
17	50%	2.4	1	3	10	7.2	106.6	1405.7	462.2
18	25%	2.34	0.75	3	10	4.3	104	1401.4	462
19	0%	0.96	2.5	3	10	3.6	103.9	1406.6	467.5

Run Number	GPC Mw	GPC Mn	GPC MWD	Mw1	Mw2	Hi/Lo Mw Ratio	Tc (onset) C	Tc (peak) C	Tg C	Tm C
15	163800	87900	1.86	-	56773	-	33.13	28.52	-44.47	43.99
16	145300	60400	2.41	163800	53056	3.06	41.88	33.94	-44.71	40.38
17	113400	45300	2.5	173465	51459	3.38	44.19	38.94	-42.80	42.65
18	84700	36300	2.33	179418	55200	3.68	47.22	42.81	-47.01	58.52
19	55200	29900	1.85	189163	-	-	50.18	46.67	-42.15	62.74

Run Number	FTIR [‡] Method	FTIR [‡] Percent Ethylene	FTIR [‡] Percent Butene	FTIR [‡] Percent ENB	Ethylene/Butene ratio	Density	%Xtal
15	EBDM	75.68	19.16	5.16	79.80/20.20	0.882	13.95
16	EBDM	75.47	19.89	4.65	79.14/20.86	0.885	15.87
17	EBDM	76.65	19.38	3.98	79.82/20.18	0.882	16.87
18	EBDM	76.98	19.75	3.27	79.58/20.42	0.886	18.29
19	EBDM	79.31	18.18	2.52	81.35/18.65	0.888	18.78

TABLE 1C

**Batch Reactor Operational Data and Physical Properties
of Ethylene/Butene/ENB Polymer and Polymer Blends**

Run Number	Percent Catalyst A	Tensile @ Break (psi)	Elongation @ Break (%)	I ₂ @ 190C/ 2.16 kg	I ₁₀ @ 190C/ 10.1 kg	I ₁₀ / I ₂ @ 190C
15	100	1142	784	0.19	1.29	6.79
16	75	1185	842	0.37	2.67	7.22
17	50	1154	908	1.03	7.86	7.63
18	25	1288	1208	3.98	31.4	7.88
19	0	1054	1052	16.2	95.3	5.89

*A - (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium 1,3-pentadiene.

B - (t-butylamido)dimethyl(2-methyl-5-indacen-1-yl)silane titanium 1,3-pentadiene.

[‡]Fourier Transformation Infrared Spectroscopy.

TABLE 1D

**Batch Reactor Operational Data and Polymer Blend Properties
of Ethylene/1-Butene Polymers and Polymer Blends**

Run Number	EB-1	EB-2	EB-3
Catalyst*	A	B	A/B
Temp, C	100.4	100.0	100.1
1-Butene, g	351.4	351.1	351.2
Ti, μ mole	1.0	0.50	0.65
B/Ti	3.0	3.0	3.0
Al/Ti	10.0	10.0	10.0
Exotherm C	10.2	5.9	4.0
C ₂ Flow, max	22.6	17.6	17.3
C ₂ rate end	0	0	0
C ₂ used, g	85.9	57.4	52.0
Calculated Efficiency	1,794,134	2,369,572	1,669,132
Solvent, g	1401.5	1406.1	1403.2
Pressure, psig	455.1	452.4	452.4
C ₂ load, g	171.8	174.2	172.5
C ₂ pressure, psig	376.5	373.8	374.5
H ₂ mmole	6.6	6.4	6.6
Mw	62,800	178,300	137,500
Mn	32,800	86,500	57,300
MWD	1.91	2.06	2.40
Mw1	-	-	69,213
Mw2	-	-	207,262
MW Ratio Hi/Lo	-	-	2.995
I ₂	10.5	0.31	0.82
I ₁₀	64.8	1.83	5.45
I ₁₀ /I ₂	6.17	5.90	6.65
Density (g/cm ³)	0.872	0.866	0.868
DSC Tm Peak Melting	56.02	37.34	32.01
% Crystallized	14.27	11.05	12.5
DSC Tg	-51.56	-53.54	-54.46
Tc (onset)	46.78	30.43	42.26
Tc (peak)	40.92	19.1	17.78
J/g	41.67	32.26	36.51

5

*A - (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium 1,3-pentadiene.

B - (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silane titanium 1,3-pentadiene.

Like the data of Table 1A, the data reported in Tables 1B, 1C and 1D shows that polymer blends made with a mixed catalyst system have a larger MWD than the polymers made under similar polymerization conditions with only one of the mixed catalyst components. This broaden MWD was obtained for elastomeric blends (that is, polymer blends of low density, for example, less than 0.89 g/cm^3) without sacrificing, and in certain cases with an improvement to, the desirable physical properties of the polymers. Moreover, the polymer blend components have a substantially uniform molecular architecture, at least with respect to the polymer units derived from ethylene and the α -olefin, because the reactivity ratios of Catalysts A and B were similar with respect to ethylene and the α -olefin as reported in Tables 7A-C.

Continuous Reactor Run Description

Ethylene/octene compositions were prepared in a continuous reactor designed for continuous addition of reactants and continuous removal of polymer solution, devolatilization and polymer recovery. Primary catalyst 1 for all samples was (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silane-titanium 1,3-pentadiene. Primary catalyst 2 for all samples was (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane-titanium 1,3-pentadiene. The primary cocatalyst for all samples was trispentafluorophenyl borane. The secondary cocatalyst for all samples was triisobutyl aluminum modified methylalumoxane.

Referring to Figure 1, ethylene, octene-1, and hydrogen were combined into single stream 10 before mixed with a diluent comprising Isopar-E to form combined feed mixture stream 11 that was continuously injected into reactor 12. Primary catalyst 1, primary catalyst 2, and a blend of the primary cocatalyst and secondary cocatalyst were combined into single stream 13 which was also continuously injected into reactor 12.

Reactor exit stream 14 was continuously introduced into separator 15 in which molten polymer was continuously separated from the unreacted comonomer, unreacted ethylene, unreacted hydrogen, and solvent. Unreacted materials 16 may be recycled to the reactor by way of combined feed mixture stream 11. The molten polymer was subsequently strand chopped or pelletized (in pelletizer 17) and after being cooled, was collected (typically as pellets).

TABLE 2**Continuous Reactor Operational Data and Polymer Blend Properties**

Run Number	20	21	22
Pilot Plant Conditions			
Primary Catalyst Ratio	50/50	60/40	50/50
Primary Catalyst 1* Feed (pph)	0.63	0.85	0.62
Primary Catalyst 2* Feed (pph)	0.63	0.56	0.62
Primary Cocatalyst Feed (pph)	0.44	0.45	0.42
Second Cocatalyst Feed (pph)	0.43	0.52	0.48
Primary Catalyst 1 Conc. (ppm)	10	10	10
Primary Catalyst 2 Conc. (ppm)	10	11	10
Primary Cocatalyst Conc. (ppm)	1250	1404	1250
Secondary Cocatalyst Conc. (ppm)	125	125	125
Primary Cocatalyst molar ratio	4.0	4.9	3.91
Second Cocatalyst molar ratio	7.36	9.6	8.4
Reactor temperature (C)	80.9	81.3	88.9
Reactor Pressure (psi)	476.5	469.1	474.3
Ethylene Feed (pph)	30.1	30.3	29.0
Octene Feed (pph)	35.1	36.2	28.9
Ethylene Conversion (%)	78.7	81.0	82.7
Solvent flow (pph)	359.6	379.9	243
Solids (%)	9.8	9.9	13.1
Production Rate (pph)	39.5	42.0	37.6
Product Properties			
Mooney	49.9	54.7	33.1
Mw1 (weight ave. mol. wt.)	262976	267269	208088
Mw2 (weight ave. mol. wt.)	88310	90245	70390
Mw1/Mw2	2.98	2.96	2.96
Overall Mw (weight ave. mol. wt.)	183377	188425	148463
Mw/Mn	2.83	2.75	2.76
190C Viscosity @ 0.1 rad/sec	453300	568590	289730
190C Viscosity @ 100 rad/sec	27837	31714	22092
Rheology ratio (0.1/100)	16.28	17.93	13.11
Density (g/cm ³)	0.8657	0.8675	0.8705
DSC peak cooling point (C)	38.85	40.76	45.69
DSC peak melting point (C)	52.89	56.25	54.98

Table 2 shows the ratio of primary catalyst 1 to primary catalyst 2, primary catalysts 1 and 2 feed in pounds per hour (pph), primary and secondary cocatalyst feeds in pph, catalyst component concentrations in parts per million parts of metal (ppm), catalyst molar ratios of cocatalyst metal species (B or Al) to total metal (Ti) concentration in the catalyst, reactor temperature in degrees Centigrade, reactor pressure in psi, solvent flow rates in pph, and ethylene (C₂) and octene (C₈) in pph. Table 2 also shows the percent conversion of ethylene, percent polymer or solids in the reactor, polymer production rate in pph, and polymer properties (Mooney, molecular weight, rheology, density and DSC data). Hydrogen was not used in these runs.

The data reported in Table 2 clearly demonstrate that the mixed catalyst systems produce broad MWD polymer blends in an efficient and facile manner. This was illustrated further by the viscosity shear rate curve at 190 C of Figure 2, and the Gottfert Rheotens data of Figure 3.

Figure 2 shows a 190 C viscosity versus frequency (rad/sec) relationship for two polymers and one polymer blend each of about 30 Mooney viscosity measured at 125 C. One of the polymers was produced using primary catalyst 1, and the other was produced using primary catalyst 2. Both of these polymers were of a narrower MWD (about 2.0) as compared to the polymer blend produced using a mix of primary catalysts 1 and 2 (that is, a mixed CGC system). Since the mixed CGC system produced a polymer blend with a broader MWD than either of the blend components, Figure 2 reports a higher shear thinning behavior (that is, the rate of change in viscosity at different shear rates). This means that the polymer blend will process through fabrication equipment better (for example, more will process through a given piece of equipment per unit of time at fixed conditions) than its individual components.

Figure 3 also reports the comparison between two products having about 30 Mooney viscosity. One of the two products was made using primary catalyst 1, and the second was made using a mixed CGC system of which one of the components was primary catalyst 1. In spite of the two polymers having similar a Mooney viscosity, the maximum melt strength (force) of the polymer blend prepared using the mixed CGC system was 10 cN versus 7 cN for the polymer prepared using primary catalyst 1. This figure demonstrates that the polymer blend produced using a mixed CGC system has higher melt strength as compared to a polymer of similar Mooney viscosity made with only one component of the system. Such polymer blends exhibit better processing

properties for applications requiring higher melt (or green) strength, for example, calendering, blow molding and thermoforming.

Moreover, the polymer blend components have a substantially uniform molecular architecture as evidenced by the single DSC melting and cooling points (the melting peak
5 tends to be broader at the lower densities). Again, this was consistent with the similarity in reactivity ratios of catalysts A and B with respect to ethylene and 1-octene as reported in Table 7A.

Crosslinking Data

10 Primary catalyst 1 for all samples was (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silane-titanium 1,3-pentadiene. Primary catalyst 2 for all samples was (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane-titanium 1,3-pentadiene.

The crosslinked elastomers identified in Table 3 below were prepared by melt blending the polymer blend of Run 22 (reported in Table 2) at 90 C in a Haake rheometer
15 equipped with a 310 cc mixing bowl and Banbury style rotors. The peroxide was added to the polymer melt and mixed at 40 rpm for 2-3 minutes. The blended compositions were removed from the Haake bowl and used to produce compression-molded plaques. The plaques were compression molded and crosslinked at 177 C for T90 plus 2 minutes to ensure full cure. Plaques were removed and immersed in a water bath until cool per
20 ASTM D-3182. ASTM test samples were then cut from the plaques for testing.

The results were also reported in Table 3 and as was evident from these results, the plaques made with the mixed catalyst system exhibit comparable to better physical properties than the plaques made from one of the catalyst components alone. Enhanced properties include those of tear strength, tensile (break and yield) and trouser tear.

TABLE 3

Physical Properties of Crosslinked Ethylene/1-Octene 30 Mooney Elastomers

Sample Number	23	24	25	26	27	28	29	30	31
	Primary Catalyst 2*			Primary Catalyst 1*			Dual Catalyst*		
DICUP® ADDITION (pph)	1.5	2.5	3.5	1.5	2.5	3.5	1.5	2.5	3.5
POLYMER weigh-up	200	200	200	200	200	200	200	200	200
PEROXIDE weigh-up	3	5	7	3	5	7	3	5	7
Shore A Hardness ASTM D-2240									
1 second	67.6	67.5	66.8	68.8	68.4	67.7	72.6	70.8	71.4
10 second	65.2	65.0	64.3	66.3	65.9	65.4	70.3	68.6	69.1
Density ASTM D-792 at 23°	0.870	0.871	0.871	0.871	0.870	0.871	0.871	0.872	0.873
Tensile @ 20 in./min ASTM D-638									
Tensile @ Break (psi)	872	597	502	953	650	543	993	759	566
Ult. Elongation (%)	582	444	357	624	460	378	588	447	332
Tensile @ Yield (psi)	172	158	162	190	158	140	224	185	192
Elong @ Yield (%)	29	27	28	31	24	20	34	26	28
Young's Modulus (psi)	872	940	939	799	962	1014	910	1097	1191
Toughness (lbs-in.)	83	54	39	99	60	45	96	67	45
100% Modulus (psi)	289	286	291	305	306	310	336	340	341
Type C Tear ASTM D-624									
Tear Strength (pli)	187.90	163.60	134.00	184.30	177.90	147.60	214.50	194.70	177.30
Total Energy (in.-lbs)	57.72	37.12	21.52	53.94	45.12	22.43	64.92	42.75	29.13
Trouser Tear ASTM D-624									
Tear Strength (pli)	22.40	18.30	12.40	28.90	14.20	11.60	35.20	22.00	14.70
Total Energy (in.-lbs)	11.37	9.11	3.95	13.60	5.37	4.37	19.48	8.33	3.91
ODR @ 177 C ASTM D-2084									
Min Torque	9.40	10.22	10.34	8.96	9.70	10.96	11.47	10.64	11.36
Max Torque	60.03	68.20	79.12	57.83	71.71	79.24	72.08	73.85	82.09
Delta	50.63	57.98	68.78	48.87	62.01	68.28	60.61	63.21	70.73
T2	0.49	0.57	0.43	1.04	1.01	0.52	1.04	0.48	0.57
T90	5.09	5.09	4.35	5.35	5.08	4.44	4.56	4.35	4.33

Thermoplastic Olefin (TPO) Applications

The polymer blends identified in Table 4 were mixed in the reported ratios, and then tumble blended in a 5-gallon bucket to assure good dispersion of all ingredients. The polymer blends were then melt blended in a ZSK 30 millimeter Werner Pfleiderer, corotating, twin-screw extruder equipped with a screw configuration that had basic kneading blocks followed by gear mixer flights to produce a medium shear, high mixing configuration. The extruder operated at a melt temperature of approximately 240 C and a speed of 200 rpm. The melt blends were passed through a 100 F water bath, chopped into granules, and collected for injection molding.

TABLE 4

TPO Formulations of Elastomers Made With a Mixed Catalyst System

Sample Number	32	33	34	35	36	37
Accpro 9934* ¹ (35 melt index)	70	70	-	-	-	-
Profax 6323* ²	-	-	70	63	70	63
Run 22 Polymer Blend (33 Mooney)	30	-	30	27	-	-
Run 20 Polymer Blend (52 Mooney)	-	30	-	-	30	27
AG 101 talc* ³	-	-	-	10	-	10
Irganox 1076* ⁴	0.2	0.2	0.2	0.2	0.2	0.2

*¹Propylene homopolymer having a density of 0.90 g/cc and I₂ of 35 g/10 min at 230 C, available from Amoco.

*²Propylene homopolymer having a density of 0.90 g/cc and I₂ of 12 g/10 min at 230 C, available from Montel.

*³Available from Microtuff Specialty Minerals

*⁴Phenolic antioxidant available from Ciba Specialty Chemicals.

ASTM samples were prepared by injection molding on a Arburg Model 370C-800-225 (800 kilonewton (kN) hydraulic clamping force) reciprocating screw injection molding machine. Molding temperatures for the barrel were set at 250 F (feed), 385, 430, 440 and 430 F (barrel through nozzle) while the mold temperature was 88 F. Injection cycles were approximately 1.75 seconds injection, 30 seconds holding and 20 seconds cooling. The hold pressures were approximately 600 bars and the velocities and pressures were adjusted as needed to completely fill mold cavities.

ASTM standard procedures were used to evaluate the molded samples. In addition, notched Izod values were obtained using an Izod impact tester and a low speed notcher equipped with a 10 mil (0.25 mm) wheel in accordance with ASTM D-256. Unnotched weldline Izod samples were cut from the middle of a double gated tensile bar and tested on the Izod impact tester. Test results were reported in Table 5. The Izod impact values were measured in units of foot-pounds per square inch (fpsi). Tensile strengths were measured in units of pounds per square inch (psi).

TABLE 5

**Physical Properties of TPO Formulations of Elastomers
Made With a Mixed Catalyst System**

Sample Number	32	33	34	35	36	37
Shore D Hardness ASTM D-2240						
1 second	66.9	66.3	61.6	64.5	63.8	65.4
10 second	64.3	63.7	58.1	61.2	60.8	62.3
Tensile @ w in./min ASTM D-6382						
Tensile @ Break (psi)	2878	2542	2790	2583	3259	2665
Ult. Elongation (%)	25	65	577	351	534	194
Tensile @ Yield (psi)	3267	2972	2718	2495	2861	3242
Elong @ Yield (%)	4	5	14	7	8	6
Rheometry (dg/10 min) ASTM D-1238						
1 ₂ @ 230 C/2.16 kg	14.4	10.7	5.9	5.6	5.7	4.5
Weld Line @ 2 in./min ASTM D-638						
Tensile @ Break (psi)	2139	2568	1984	1915	2370	2088
Ult. Elongation (%)	1	3	3	1	8	3
Tensile @ Yield (psi)	2131	2562	1982	1912	2406	2079
Elong @ Yield (psi)	1	3	3	1	6	2
3-Point Flex ASTM D-790						
Flex Modulus (psi)	168900	155576	102315	170010	112305	172583
2% Secant Modulus (psi)	154042	142289	93316	137421	103310	141590
Gloss ASTM D-523						
20°	35.1	16.8	67.8	45.9	27.5	36.3
60°	51.2	30.9	82.3	68.9	66.6	67.6
85°	84.3	79.1	98.8	95.3	92.1	91.5
Dynacup Total Energy (ft lb)						
23 C	27.9	27.7	26	27.2	31	32.3
-30 C	26.6	25.9	39.4	24.5	36.1	17.0
Izod Impact Strength (ft lbs/in.)						
23 C	1.54	1.64	14.39	12.03	13.89	12.3
0 C	1.48	1.16	9.93	5.34	1.85	2.25
RT Weldline Izods (ft lbs/in.)						
23 C	1.74	3.95	5.85	2.56	7.66	2.49
Heat Distortion @ 66 psi						
HDT in C	99.5	91.7	80.3	78.9	77.5	81.2

The data reported in Table 5 shows a unique balance of rheometry, modulus, impact strength, and weld line strength important for TPO automotive applications.

Blend of TPO and a Medium Mooney Viscosity Ethylene/1-Octene Polymer Blend

5 Medium Mooney viscosity, for example, 35-55, polymer blends of ethylene and 1-octene (that is, an ethylene/1-octene copolymer made with a mixed CGC system and of substantially uniform molecular architecture) yield a superior combination of tensile strength, toughness, scuff or abrasion resistance, color stability and thermoformability than that obtainable either with a medium Mooney viscosity EPDM or a low Mooney
10 viscosity, for example, less than 35, conventional ethylene/1-octene copolymer (that is, a nonblended copolymer) when blended with a TPO. Such TPO blends were useful in many thermoforming operations, for example, the manufacture of automotive instrument panel skins.

The following TPO blends were mixed in a Haake 230 cm³ mixing bowl fitted
15 with roller blades:

TABLE 6A
TPO Blends

Blend	38	38-C1	38-C2
Profax 6323	25	25	25
Surlyn 9520	27	27	27
Elvaloy AS	3	3	3
Nordel 3681	0	45	0
ENGAGE 8150	0	0	45
EO Polymer Blend	45	0	0

20 Profax 6323, available from Montel, was a propylene homopolymer having a density of 0.90 g/cc and a melt flow index of 12 grams/10 min. at 230°C. Surlyn 9520, available from DuPont, was an ethylene/methacrylic acid copolymer partially neutralized with zinc, having a melt index of 1.1 and a specific gravity of 0.95 g/cc. Elvaloy AS, also supplied
25 by DuPont, was an ethylene/n-butyl acrylate/glycidyl methacrylate copolymer with a melt index of 12 g/10 min and a specific gravity of 0.94 g/cc. Nordel 3681, produced by DuPont Dow Elastomers, L.L.C., was an ethylene/propylene/diene terpolymer using 1,4 hexadiene as the diene monomer, having 71 wt. percent ethylene with a nominal 52 ML(1+4) Mooney viscosity and was polymerized via a vanadium based catalyst.
30 ENGAGE 8150 was an ethylene/1-octene copolymer with a density of 0.868 g/cc, a

nominal melt index of 0.5 g/10 min at 190°C, and a nominal Mooney viscosity of 45 ML (1+4). It was polymerized with t-butylamido) dimethyl (tetramethylcyclopentadienyl) silanetitanium 1,3-pentadiene. EO polymer blend was an ethylene/1-octene copolymer with a density of 0.868 g/cc and a nominal Mooney viscosity of 45 ML (1+4), and it was
5 polymerized via a 50/50 wt./wt. ratio of t-butylamido)dimethyl(tetramethylcyclopentadienyl)silanetitanium 1,3-pentadiene and t-butylamido)dimethyl(2-methyl-s-undacen-1-yl)silanetitanium 1,3-pentadiene. Melt index was measured in accordance with ASTM D1238. Mooney viscosity was measured in accordance with ASTM D1646.

10 The following mix procedure was used:

- 1) Set Haake bowl to 190 C, split signal from melt thermocouple to control Thermocouple for bowl.
- 2) Start initially at 30 rpm, add all polymers, except for Elvaloy AS, to bowl.
- 15 3) Increase speed to 75 rpm
- 4) Mix for five minutes, then add Elvaloy AS and mix for four minutes.
- 5) Remove melt from bowl and press out into crude plaques using a 32 mm thick
Mold at 190 C for three minutes at 18,200 Kg pressure, then cool for three
20 Minutes at 18,200 Kg pressure.

The samples were then compression molded into 15.2 cm x 25.5 cm x 1.5 mm thick plaques using the following compression cycle:

- 1) 3 minutes preheat at 210 C, no pressure.
- 25 2) 3 minutes at 18,200 Kg, 210 C.
- 3) 3 minutes at 18,200 Kg, cooling.

Sample hardness was tested according to ASTM D 2240. Tensile properties were tested according to ASTM D 638. Tear properties were tested in accordance with ASTM D 624.

30 Abrasion resistance was measured according to ASTM D 1630.

Elevated temperature stress-strain measurements give an indication of how the compound with thermoform at elevated temperature. During sheet thermoforming, the compound must exhibit optimum stress-strain behavior. A very stiff product will not yield under vacuum. On the other hand, the sheet at the forming temperature must exhibit
35 enough stress response to minimize thin spots during the forming operation. Tensile properties at 140 C were measured by cutting tensile samples from an ISO T2 die. These

samples were placed in a tensile tester fitted with an environmental chamber heated to 140 C. The tensile samples were strained at a rate of 50 cm/min. Strain was measured via an optical extensometer.

5

TABLE 6B**TPV Blend Properties**

Property	38	38-C1	38-C2
Shore D Hardness 1 second	42.8	45.0	38.3
Tensile @ 7.9 cm/min Tensile @ Break (Mpa)	12.9	8.9	12.2
Ult. Elongation (%)	435	262	486
Type C Tear Tear Strength (PLI)	398	295	374
NBS Abrasion Index	71	58	49
Hot Stress-strain @ 140 C Max Eng. Stress, Mpa	0.306	0.354	0.235
True Stress @ 500% elong., Mpa	1.78	1.88	1.38

As can be seen from the results reported in Table 6B, Comparative Example 38-C1, which contains Nordel 3681, contains lower ultimate tensile and elongation than either Comparative Example 38-C2 or Example 38, both containing ethylene/1-octene copolymers. However, Comparative Example 38-C1 exhibits acceptable stress-strain characteristics at 140 C. Note that Example 38 exhibits tensile stress at 140 C much closer to Comparative Example 38-C1 than does Comparative Example 38-C2. Example 38 was much more suitable for vacuum thermoforming than Comparative Example 38-C2. Further, note that Example 38 exhibits significantly higher abrasion resistance than either of the two comparative examples. Thus, Example 38 exhibits a unique combination of high ultimate tensile strength, elongation, abrasion resistance and high elevated temperature tensile stress, making it especially suitable for automotive interior.

20

Tape Extrusion Comparison

A 30 Mooney polymer produced with catalyst A ((t-butylamido)dimethyl-(tetramethylcyclopentadienyl)silane)titanium 1,3-pentadiene) was compared to a 30 Mooney polymer produced with a mixed catalyst A + catalyst B ((t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silane)titanium 1,3-pentadiene) in a extruded tape test. Both polymers were extruded on a 2½ inch 30/1 L/D Killion extruder

25

having a barrier ET screw. Dimensions of the tape die were 1.5 inches wide and 0.06 inches thick. The extruder temperature profile was: feed 100°C, 176°C, 204°C, 204°C, 204°C, and 204°C at the die. The extruder was run at 35 rpm and 35 pounds per hour. Results from this test indicated sever melt fracture on the tape made with the polymer produced by catalyst A while the tape made from the polymer produced by the mixed catalyst system of A and B showed no evidence of melt fracture.

Reactivity Ratios

Reactivity ratios for propylene, butene, 1-octene and ENB were reported in Tables 7A-C. These ratios were based on the data reported for runs 1, 3, 4, 6-8, 10, 14-15 and 19. All the values assumed r_2 was equal to 0.5.

TABLE 7A
Ethylene/Octene Copolymer

Run Number	Catalyst Code	Reactor Temp C	Polymer Composition		
			C ₂ wt %	C ₈ Wt %	r ₁ value
1	A	90	64.59	35.41	3.5
3	B	90	65.17	34.83	3.6
4	A	110	64.91	35.09	5.1
6	B	110	58.40	41.60	3.8
7	B	110	45.50	54.50	3.3
8	C	110	76.00	24.00	14.3

- *A - (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium 1,3-pentadiene.
 B - (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silane titanium 1,3-pentadiene.
 C - [N-(1,1-dimethylethyl)-1,1-dimethyl-1-((1,2,3,3a,7a-h)-3-(1-pyrrolidinyl)-1H-inden-1-yl)silanamino-(2-)-N] [(2,3,4,5,-h)-2,4-pentadiene)]-titanium.

As reported in Table 7A, the reactivity ratios for catalysts A and B were essentially the same, that is, within 5 percent, for ethylene/1-octene polymerization at 90 C. At the higher temperature of 110 C, the reactivity ratios were still similar, for example, within 35 percent. The reactivity ratios for catalysts B and C at 110 C were, in contrast, very different with the reactivity ratio for catalyst C 4.33 times greater than that of catalyst B. The large difference in reactivity ratio was evident in the fact that polymerization with catalyst C yielded a polymer with less than half the amount of 1-octene incorporated into it as was incorporated into it with catalyst B.

TABLE 7B
EPDM Terpolymers

Composition						
Run Number	Catalyst Code	C ₂ wt %	C ₃ Wt %	ENB Wt %	r _l value for C ₃	r _l value for ENB
14	A	66	30.2	3.9	2.8	5.5
10	B	67.1	26.2	6.7	3.5	3.6

As reported in Table 7B, the reactivity ratios for ethylene/propylene polymerization at 100 C were similar for catalysts A and B, that is, within 25 percent of each other. The reactivity ratios for ethylene/ENB, in contrast, were further apart, that is, 52 percent.

10

TABLE 7C
EBDM Terpolymers

Composition						
Run Number	Catalyst Code	C ₂ wt %	C ₄ Wt %	ENB Wt %	r _l value for C ₄	r _l value for ENB
19	A	79.31	18.18	2.52	7.3	8.7
15	B	75.68	19.16	5.16	6.4	4.2

As reported in Table7C, the reactivity ratios for ethylene/butene polymerization at 100 C with catalysts A and B were very similar, with 14 percent of one another. In contrast, the reactivity ratios for ethylene/ENB at 100 C with catalysts A and B were very different, with the reactivity ratio of catalyst A more than twice that of catalyst B.

For comparative purposes, Kaminsky and Schlobohm report in Makromol. Chem., Makromol. Symp., 4, 103-18, 1986, that the reactivity ratio r_l of bis(cyclopentadienyl)zirconium dichloride (a sandwich type zirconium compound) for ethylene polymerization with butene at 85 C was 125, more than 17 times that of catalyst A at 100 C.

Although the invention has been described in considerable detail through the specification and examples, one skilled in the art can make many variations and modifications without departing from the spirit and scope of the invention as described in the following claims.

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CLAIMS:

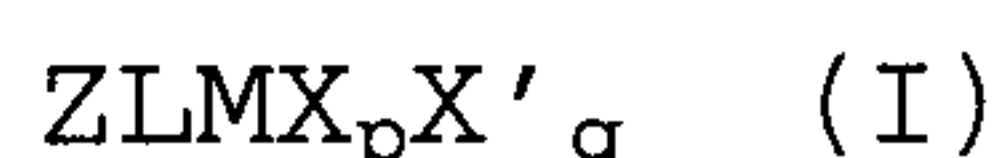
1. An ethylene-based polymer blend having (a) a molecular weight distribution (i) of at least 2, and (ii) at least ten percent greater than that of a polymer prepared in a single reactor with either the first or second catalyst alone under similar polymerization conditions, and (b) a uniform molecular architecture, the polymer blend prepared by a process comprising contacting under polymerization conditions and in a single reaction vessel:

A. ethylene,

B. at least one C₃-C₂₀ α-olefin, and

C. a mixed catalyst system comprising a first catalyst and a second catalyst, and each catalyst comprising:

1. a metal complex of formula I



wherein M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4 bound in an η^5 bonding mode to L;

L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least the divalent moiety, Z, and L further may be substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino and silyl groups containing up to 20 nonhydrogen atoms;

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Z is a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements,
5 and also comprising nitrogen, phosphorus, sulfur or oxygen;

X is an anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently in each occurrence is a neutral
10 ligating compound having up to 20 atoms;

p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that when X is a dianionic ligand group, p is 1; and

q is 0, 1 or 2; and

15 2. an activating cocatalyst;

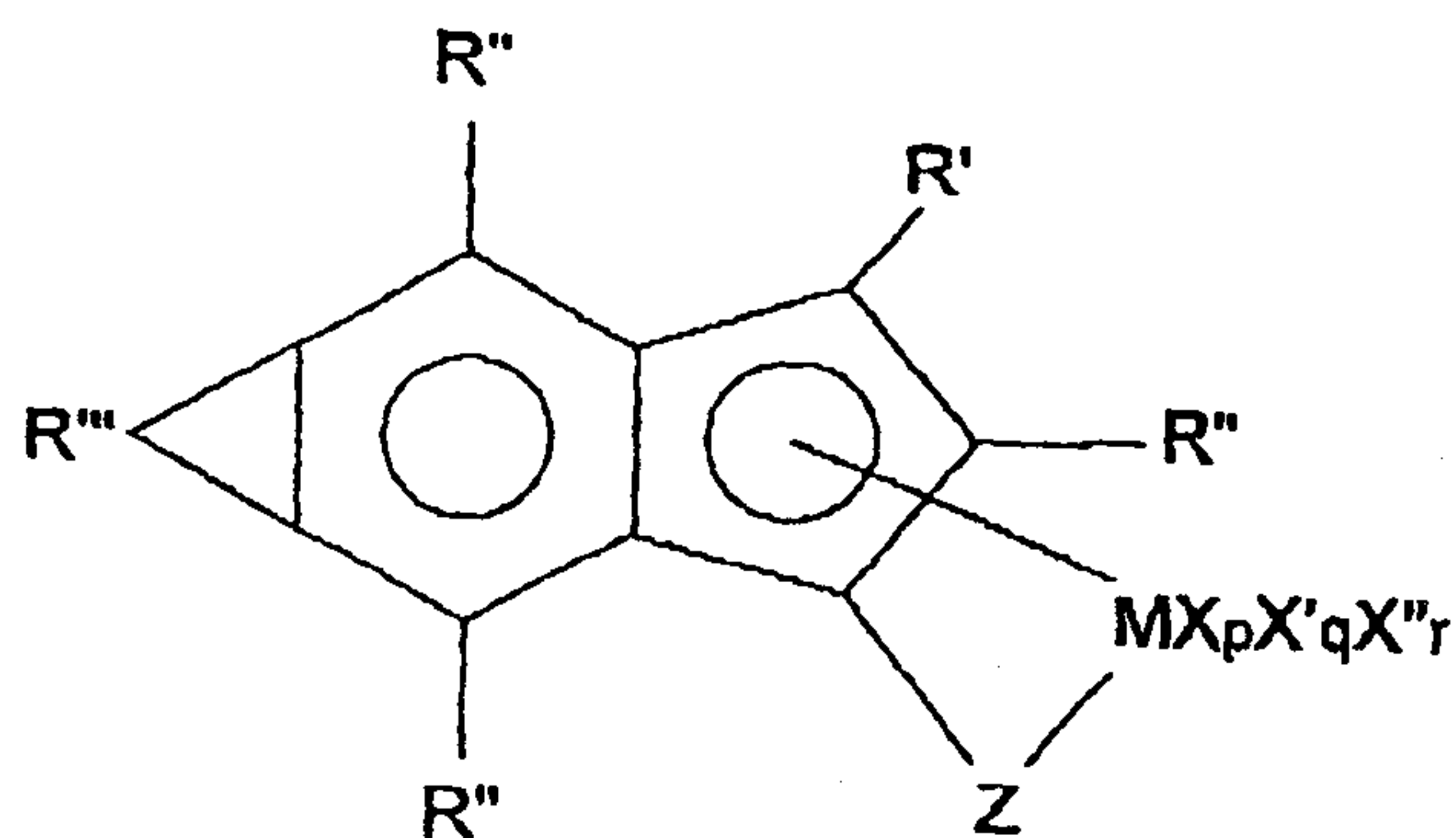
with the provisos that

D. the first catalyst is different from the second catalyst, and

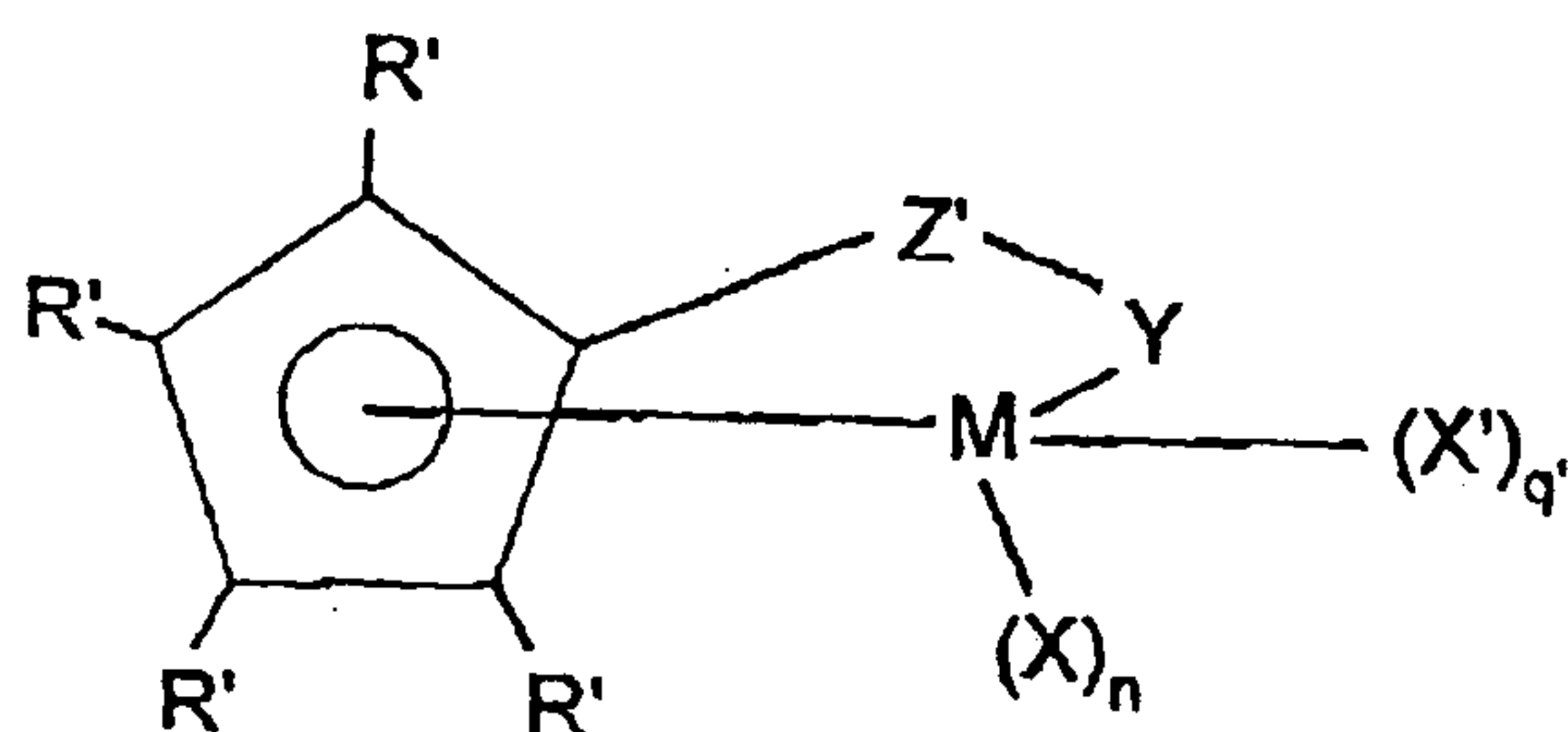
E. the weight ratio of the first catalyst to the
20 second catalyst, based on the weight of the metal M in each catalyst, is between 90:10 and 10:90.

2. The polymer blend of claim 1 in which each catalyst of the process for making the polymer blend comprises a metal complex of the formula:

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or



in which M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

R' and R'' are independently each occurrence hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbyl-sulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said R' or R'' group having up to 40 nonhydrogen atoms, and optionally two or more of the foregoing groups may together form a divalent derivative;

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R''' is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said R''' containing from 1 to 30 nonhydrogen atoms;

5 X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence is a neutral ligating compound having up to 20 atoms;

10 X'' is a divalent anionic ligand group having up to 60 atoms;

Y is a divalent ligand group comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 nonhydrogen atoms, Y is also bonded to Z and M through the nitrogen,
15 phosphorus, oxygen or sulfur, and optionally Y and Z together form a fused ring system;

Z is a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said Z comprising boron, or a
20 member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

Z' is SiR^*_2 , CR^*_2 , $\text{SiR}^*_2\text{SiR}^*_2$, $\text{CR}^*_2\text{CR}^*_2$, $\text{CR}^*=\text{CR}^*$, or $\text{CR}^*_2\text{SiR}^*_2$;

R* each occurrence is independently selected from
25 the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 nonhydrogen atoms,

and mixtures thereof, or two or more R* groups from Y, Z', or from Z' together with Y form a fused ring system;

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n is 0, 1 or 2;

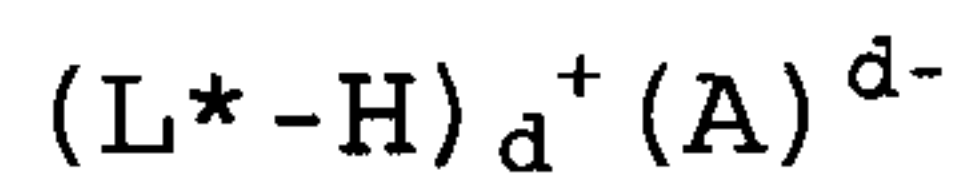
p is 0, 1, 2, or 3;

q is 0, 1 or 2;

q' is 0 or 1; and

5 r is 0 or 1.

3. The polymer blend of claim 1 in which the activating cocatalyst of the process for making the polymer blend is at least one of the formula:



10 in which

L* is a neutral Lewis base;

(L*-H)⁺ is a Bronsted acid;

A^{d-} is a noncoordinating, compatible anion having a charge of d-; and

15 d is an integer of 1-3.

4. The polymer blend of claim 3 in which the activating cocatalyst is at least one of trispentafluorophenyl-borane and at least one of a modified methylalumoxane.

20 5. The polymer blend of claim 3 in which the activating cocatalyst of the first catalyst is the same as the activating cocatalyst of the second catalyst.

6. The polymer blend of claim 3 in which the activating cocatalyst of the first catalyst is different
25 than the activating cocatalyst of the second catalyst.

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7. The polymer blend of claim 3 in which the activating cocatalyst comprises N,N-di(n-hexadecanyl)-N-methylammonium tetrakis(2,3,4,5,6-pentafluorophenyl) borate.

5 8. The polymer blend of claim 3 in which the activating cocatalyst comprises a combination of (i) N,N-di(n-hexadecanyl)-N-methylammonium tetrakis(2,3,4,5,6-pentafluorophenyl) borate, (ii) tris(pentafluorophenyl) borane, and (iii) a modified
10 methylalumoxane.

9. The polymer blend of claim 3 in which the α -olefin is at least one C₃-C₈ α -olefin.

10. The polymer blend of any one of claims 1 to 9 in combination with a thermoplastic olefin.

15 11. The polymer blend of claim 10 in which the thermoplastic olefin is polypropylene homopolymer or polypropylene copolymer.

12. The polymer blend of any one of claims 1 to 11 which is at least partially crosslinked.

20 13. The polymer blend of any one of claims 1 to 12 in which the rheology ratio is greater than that of a polymer blend component of substantially the same Mooney viscosity and prepared in a single reactor with either the first or second catalyst alone under similar polymerization
25 conditions.

14. The polymer blend of claim 13 in which the I₂ is less than 0.5.

15. The polymer blend of claim 13 in which the Mooney viscosity is greater than 35.

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16. The polymer blend of any one of claims 1 to 15 further comprising at least one of a filler, oil, plasticizer, colorant, UV-stabilizer, antioxidant, peroxide, blowing agent, metal release agent or reinforcing agent.

5 17. An ethylene-based polymer blend having an MWD (a) of at least 2, and (b) at least ten percent greater than any ethylene-based polymer component of the blend prepared in a single reactor with any single component of the mixed catalyst system under similar polymerization conditions, and
10 (b) a uniform molecular architecture, the polymer blend prepared by a process comprising contacting under polymerization conditions and in a single reaction vessel:

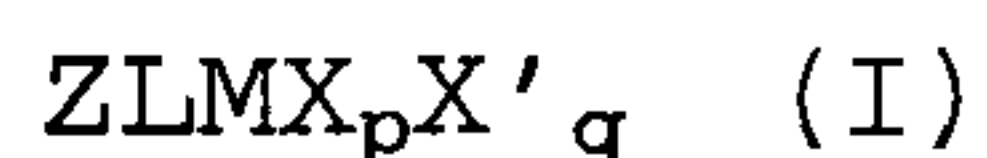
A. ethylene,

B. at least one C₃-C₂₀ α-olefin,

15 C. at least one polyene, and

D. a mixed constrained geometry catalyst (CGC) system comprising a first catalyst and a second catalyst, each catalyst having substantially the same reactivity ratio with respect to at least one C₃-C₂₀ α-olefin of B, and each
20 catalyst comprising:

1. A metal complex of formula I,



wherein M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or
25 +4 bound in an η⁵ bonding mode to L;

L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl-group covalently substituted with at least the divalent moiety, Z, and L further may be

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substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino and silyl groups containing up to 20
5 nonhydrogen atoms;

Z is a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements,
10 and also comprising nitrogen, phosphorus, sulfur or oxygen;

X is an anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently in each occurrence is a neutral
15 ligating compound having up to 20 atoms;

p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that when X is a dianionic ligand group, p is 1; and

q is 0, 1 or 2; and

20 2. an activating cocatalyst;

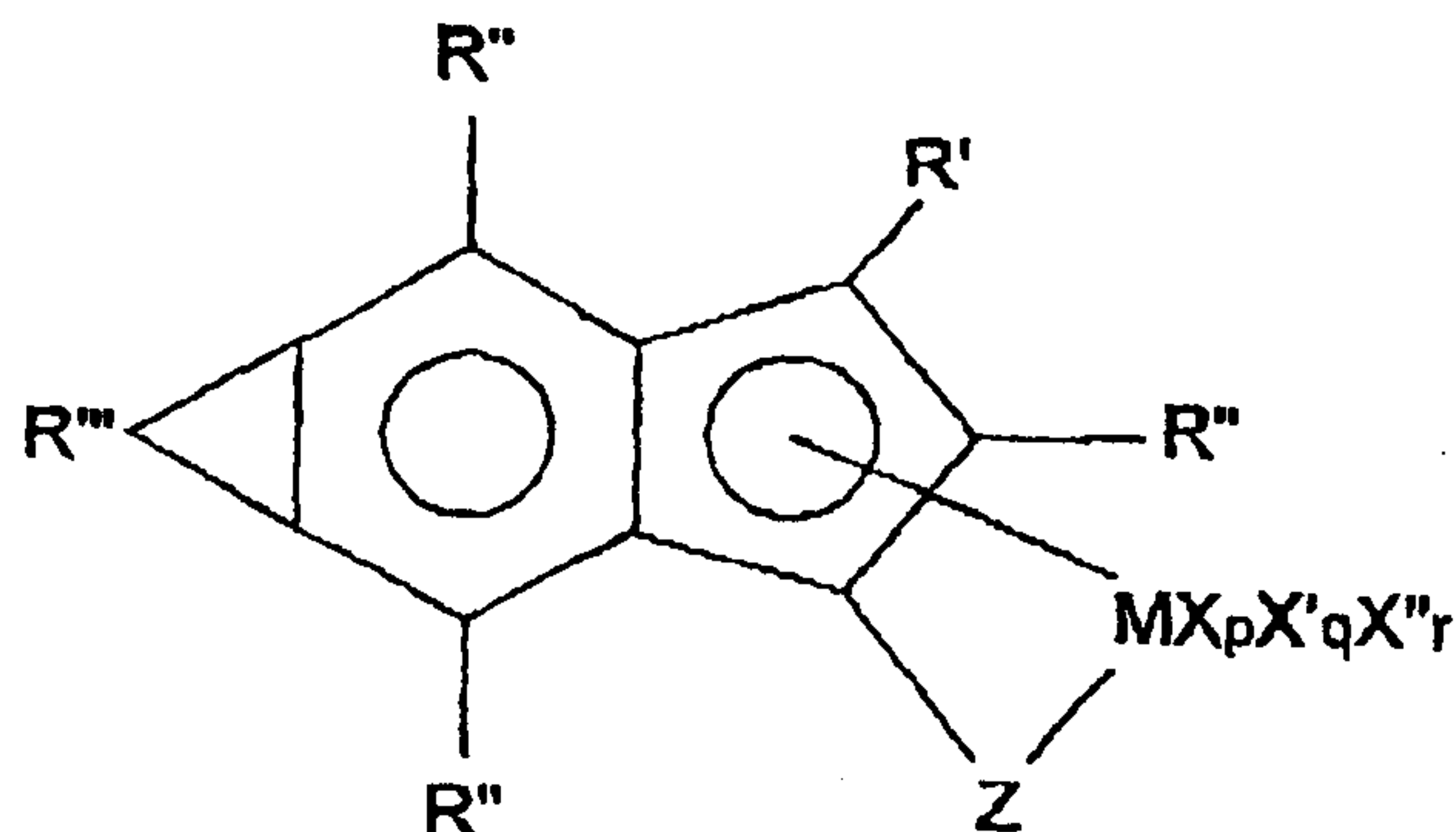
with the provisos that

E. the first catalyst is different from the second catalyst, and

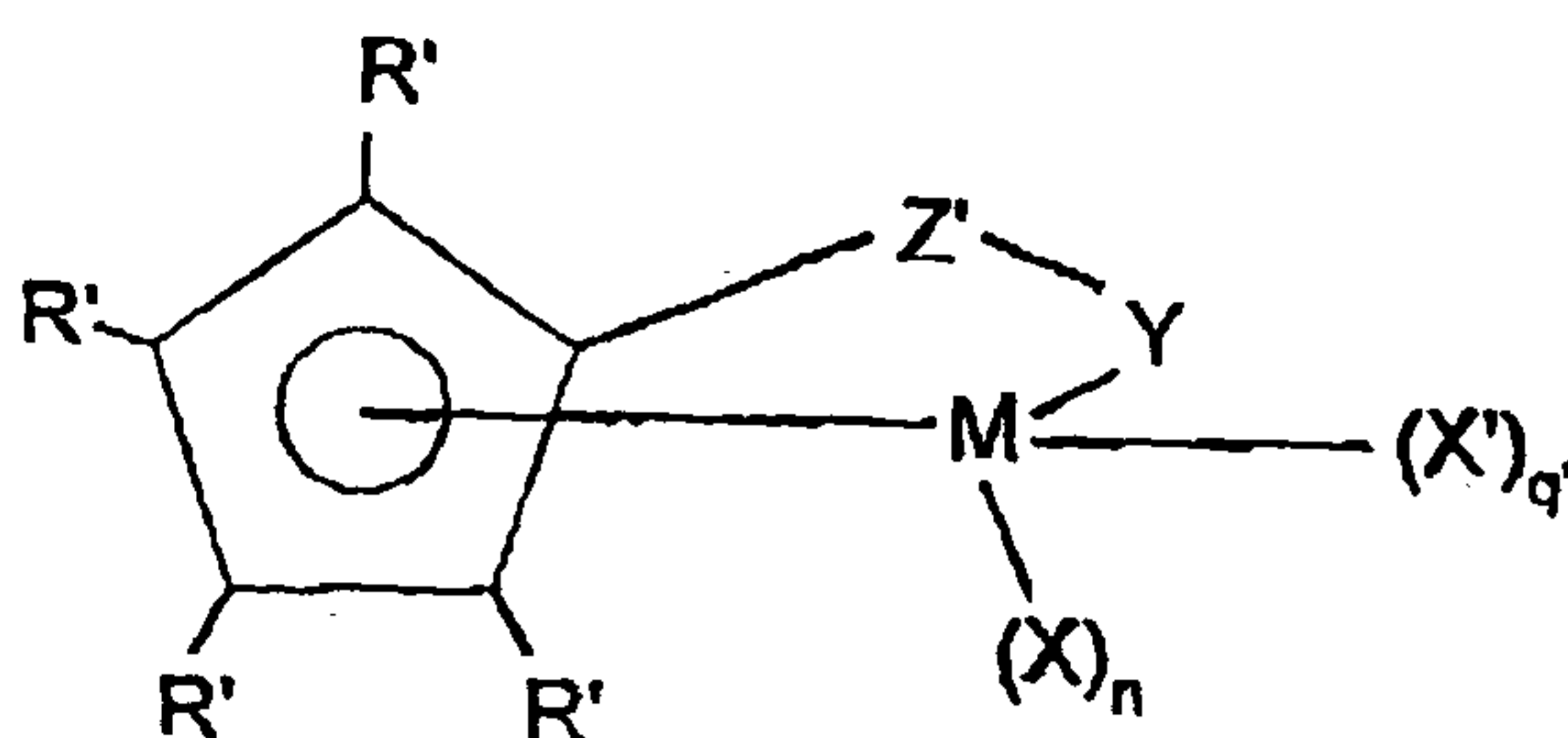
F. the weight ratio of the first catalyst to the
25 second catalyst, based on the weight of the metal M in each catalyst, is between 90:10 and 10:90.

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18. The polymer blend of claim 17 in which each catalyst of the process for making the polymer blend comprises a metal complex of the formula:



or



in which M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

R' and R'' are independently each occurrence hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbyl-sulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl,

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hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said R' or R'' group having up to 40 nonhydrogen atoms, and optionally two or more of the foregoing groups may together form a divalent
 5 derivative;

R''' is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said R''' containing from 1 to 30 nonhydrogen atoms;

10 X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence is a neutral ligating compound having up to 20 atoms;

15 X'' is a divalent anionic ligand group having up to 60 atoms;

Y is a divalent ligand group comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 nonhydrogen atoms, Y is also bonded to Z and M through the nitrogen,
 20 phosphorus, oxygen or sulfur, and optionally Y and Z together form a fused ring system;

Z is a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said Z comprising boron, or a
 25 member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

Z' is SiR^*_2 , CR^*_2 , $\text{SiR}^*_2\text{SiR}^*_2$, $\text{CR}^*_2\text{CR}^*_2$, $\text{CR}^*=\text{CR}^*$, or $\text{CR}^*_2\text{SiR}^*_2$;

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R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 nonhydrogen atoms,

5 and mixtures thereof, or two or more R* groups from Y, Z', or from Z' together with Y form a fused ring system;

n is 0, 1 or 2;

p is 0, 1, 2, or 3;

q is 0, 1 or 2;

10 q' is 0 or 1; and

r is 0 or 1.

19. The polymer blend of claim 17 in which the activating cocatalyst of the process for making the polymer blend is at least one of the formula:

15 $(L^*-H)_d^+(A)^{d-}$

in which

L* is a neutral Lewis base;

$(L^*-H)^+$ is a Bronsted acid;

20 A^{d-} is a noncoordinating, compatible anion having a charge of d-; and

d is an integer of 1-3.

20. The polymer blend of claim 19 in which the activating cocatalyst is at least one of trispentafluorophenyl-borane and at least one of a modified
25 methylalumoxane.

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21. The polymer blend of claim 19 in which the activating cocatalyst of the first catalyst is the same as the activating cocatalyst of the second catalyst.

22. The polymer blend of claim 19 in which the activating cocatalyst of the first catalyst is different than the activating cocatalyst of the second catalyst.

23. The polymer blend of claim 19 in which the activating cocatalyst comprises

N,N-di(n-hexadecanyl)-N-methylammonium tetrakis
(2,3,4,5,6-pentafluorophenyl) borate.

24. The polymer blend of claim 19 in which the activating cocatalyst comprises a combination of (i) N,N-di(n-hexadecanyl)-N-methylammonium tetrakis
(2,3,4,5,6-pentafluorophenyl) borate, (ii)

tris(pentafluorophenyl) borane, and (iii) a modified methylalumoxane.

25. The polymer blend of claim 19 in which the α -olefin is at least one C_3 - C_8 α -olefin.

26. The polymer blend of claim 17 in which the polyene is at least one of 1,3-butadiene, isoprene, 1,3-pentadiene, 7-methyl-1,6-octadiene and 5-ethylidene-2-norborene.

27. The polymer blend of claim 26 in which the polymerization conditions include liquid or suspension phase conditions and a temperature between 65 and 160°C.

28. The polymer blend of claim 27 in which the first catalyst is (t-butylamido)dimethyl(2-methyl-s-indacen-1-yl)silane titanium 1,3-pentadiene and the second catalyst is (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium 1,3-pentadiene.

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29. The polymer blend of any one of claims 17 to 28 in combination with a thermoplastic olefin.

30. The polymer blend of claim 29 in which the thermoplastic olefin is polypropylene homopolymer or
5 polypropylene copolymer.

31. The polymer blend of any one of claims 17 to 30 which is at least partially crosslinked.

32. The polymer blend of any one of claims 17 to 31 in which the rheology ratio is greater than that of a polymer
10 blend component of substantially the same Mooney viscosity and prepared in a single reactor with either the first or second catalyst alone under similar polymerization conditions.

33. The polymer blend of claim 32 in which the I_2 is
15 less than 0.5.

34. The polymer blend of claim 32 in which the Mooney viscosity is greater than 35.

35. The polymer blend of any one of claims 17 to 34 further comprising at least one of a filler, oil,
20 plasticizer, colorant, UV-stabilizer, antioxidant, peroxide, blowing agent, metal release agent or reinforcing agent.

36. An article made from the polymer blend of any one of claims 1 to 35.

37. The article of claim 36 in the form of an
25 injection-molded, a blow-molded, extruded, roto-molded, slush-molded, compression-molded, or a thermoformed part.

38. The article of claim 37 in the form of a wire or cable insulation or coating, footwear, building or construction material, an adhesive, a film or fiber,

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flooring, a foam, weather stripping, an oil modifier, an extruded sheet, an instrument panel or door panel skin, food packaging, an automotive part or an electronic part.

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FIG. 1

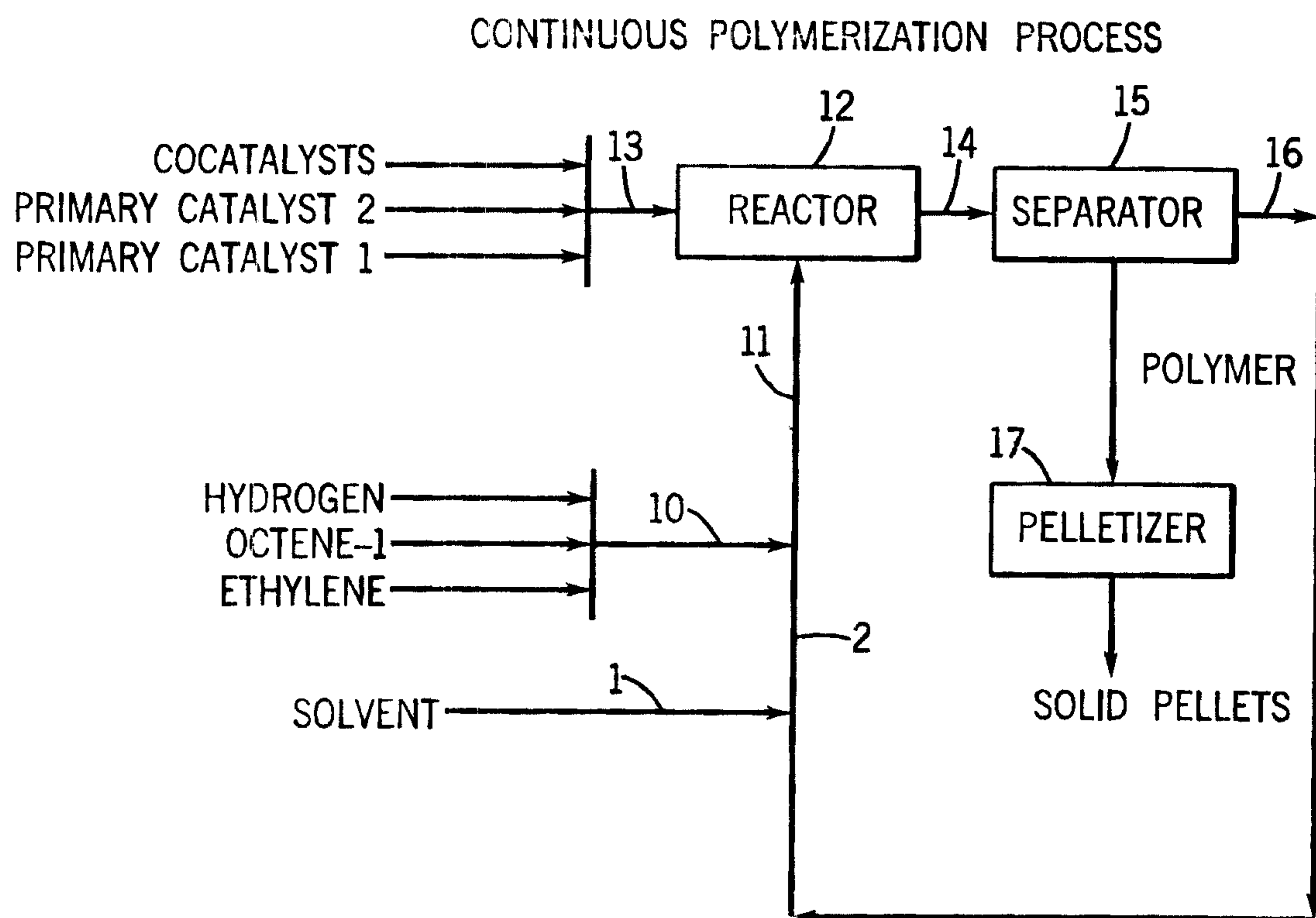
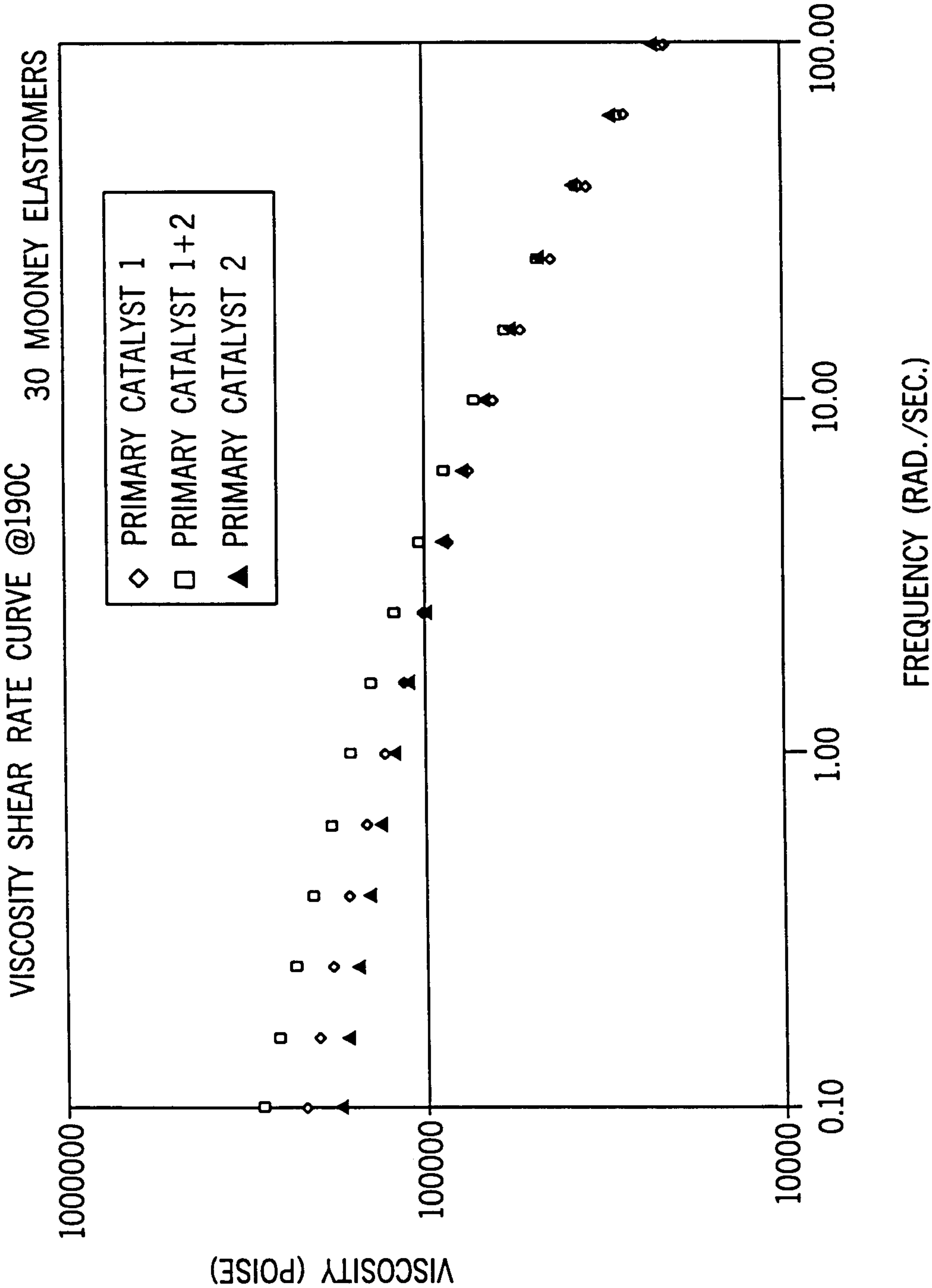


FIG. 2



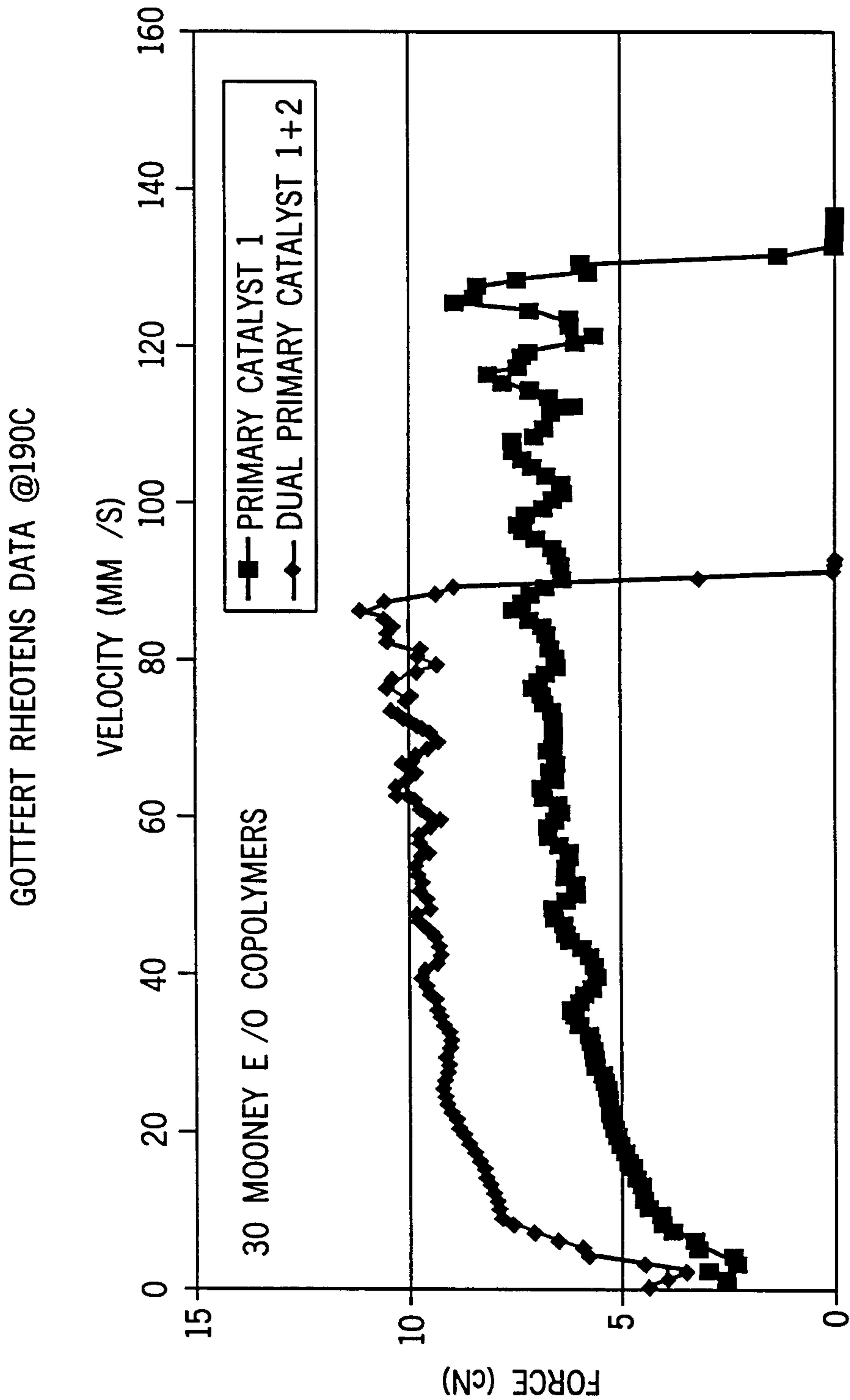


FIG. 3

CONTINUOUS POLYMERIZATION PROCESS

