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(54) Title: POLYMER LAYERED INORGANIC NANOCOMPOSITES		
(57) Abstract The present invention provides a polyolefin material comprising: a polyolefin and a layered inorganic material, in which the layered inorganic material comprises at least 1 % by weight of the polyolefin material. The present invention also provides a method for forming a polyolefin material comprising: providing at least one olefin monomer; and polymerizing the olefin monomer using an intercalated catalyst and support system to form a polyolefin material comprising a polyolefin and a layered inorganic material.		

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POLYMER LAYERED INORGANIC NANOCOMPOSITES

CROSS-REFERENCE TO RELATED APPLICATIONS

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This application makes reference to U.S. Provisional Application No. 60/134,866 entitled "Polymer Layered Inorganic (Silicate) Nanocomposites from Intercalated Transitional Metal Catalysts, filed May 19, 1999. The entire contents and disclosure of this Provisional Patent Application is hereby incorporated by reference.

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BACKGROUND OF THE INVENTION

Field of the Invention

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The present invention relates generally to polyolefin materials and methods for making polyolefin materials.

Description of the Prior Art

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Polymer layered silicate nanocomposites are novel materials that have improved mechanical, barrier, and flammability properties as compared to conventional filled polymer composites. Polymerization of monomer intercalated in the gallery space between the plate-like layers of the silicate (*in situ* polymerization) has been used to prepare exfoliated polymer layer silicate nanocomposites. However, there currently exists no method for *in situ* polymerization of polyethylene, polypropylene, or other polyolefin layered silicate nanocomposites containing a significant amount of layered silicate. Melt intercalation of polypropylene has been accomplished. One approach requires a polypropylene derivative, such as polypropylene-graft-maleic anhydride and only results in partial expansion of the silicate layers to form an intercalated ^βnanocomposite, see Hasegawa, *et al.*, *J. App. Poly. Sci.*, Vol. 67, pp. 87-92 (1998) and Gilman, *et al.*, *Fire Retardancy of Polymers: the Use of Intumescence*, The Royal

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Society of Chemistry, Cambridge, p. 203 (1998). The second melt intercalation method yields exfoliated nanocomposite, but it requires two organic treatments of the layered silicate: the ion exchange with alkylammonium cation and intercalation of hydroxy-terminated polyolefin, see Usuki, *et al.*, *J. App. Poly. Sci.*, Vol. 62, pp. 137-139 (1997).

- 5 These approaches introduce "impurities" into the nanocomposite, i.e. the maleic anhydride graft or the hydroxy-terminated polyolefin. This lowers the performance of the nanocomposite due to lower thermal stability or reduced crystallinity.

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SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method for *in situ* polymerization of polyethylene, polypropylene, and other polyolefin layered inorganic nanocomposites containing a significant amount of layered silicate.

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It is another object of the present invention to provide a polyolefin material having an improved tensile strength.

It is another object of the present invention to provide a polyolefin material
20 having an improved tensile modulus.

It is another object of the present invention to provide a polyolefin material having an improved UV stability.

25 It is another object of the present invention to provide a polyolefin material that is less subject to elongation.

It is another object of the present invention to provide a polyolefin material that is less flammable.

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It is another object of the present invention to provide a polyolefin material having less permeability.

According to a first broad aspect of the present invention, there is provided a method for forming a polyolefin material comprising: providing at least one olefin monomer; and polymerizing the olefin monomer using an intercalated catalyst and support system to form a polyolefin material comprising a polyolefin and a layered inorganic material wherein the intercalated catalyst and support system comprises a sufficient amount of the layered inorganic material so that the layered inorganic material comprises at least 1% by weight of the polyolefin material.

According to a second broad aspect of the invention, there is provided a polyolefin material comprising: a polyolefin; and a layered inorganic material, the layered inorganic material comprising at least 1% by weight of the polyolefin material.

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Other objects and features of the present invention will be apparent from the following detailed description of the preferred embodiment.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

It is advantageous to define several terms before describing the invention. It should be appreciated that the following definitions are used throughout this application.

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Definitions

Where the definition of terms departs from the commonly used meaning of the term, applicant intends to utilize the definitions provided below, unless specifically indicated.

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For the purposes of the present invention, the term "olefin" refers to any hydrocarbon or hydrocarbon derivative including one or more carbon-carbon double bonds. The term "olefin" also refers to mixtures of olefin monomers that may be copolymerized with each other. For example, the olefins that may be used to make the polyolefin material of the present invention include simple olefins such as ethylene, propene, styrene, *etc.*

For the purposes of the present invention, the term "polyolefin" refers to any polymer derived from one or more olefins. For example, polyolefins include polymers formed by polymerizing simple olefins such as ethylene, propene, styrene, *etc.* or by copolymerizing simple olefins such as ethylene, propene, styrene, *etc.*, with alpha-olefins such as 1-butene, *etc.*, with cyclic olefins such as cyclohexene, norbornylene, *etc.*, or with olefins containing alcohol, amine, amide, ester, acid anhydride and other polar functionalities.

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For the purposes of the present invention, the term "polyolefin in pure form" refers to just the polyolefin that is substantially free of impurities. In contrast, the term "polyolefin material" refers to a product including a polyolefin and other impurities, such as a layered inorganic material of the present invention.

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For the purposes of the present invention, the term "transition metal catalyst" refers to any catalyst containing a transition metal that may be used to polymerize an olefin. For example, the transition metal catalyst of the present invention may be any compound including a transition metal from Group 2 to Group 13 of the Periodic Table that has an affinity, either ionic or non-bonded, for the layered inorganic material into which the transition metal catalyst is intercalated. The transition metal in the transition metal catalyst of the present invention may be an actinide or lanthanide.

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For the purposes of the present invention, the term "layered inorganic material" refers to any layered inorganic material, either natural or synthetic. The layered inorganic material, in addition to supporting an intercalated transition metal catalyst

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may also contain 0.001 to 300 parts by weight of an organic-substituted cations or anions, or a mixture of organic substituted cations or anions. Suitable organic-substituted cations may be, but are not limited to, amine-based cations such as ammonium, imminium, sulfur-based cations, such as sulphonium, oxygen-based cations
5 such as oxonium, or phosphorus based cations, such as phosphonium. Suitable organic-substituted anions may be, but are not limited to, caboxylate, sulphate, phosphate, nitrate or aluminate anions. The organic-substituted cations or anions may be associated with anions which reside in the layered inorganic material.

10 For the purposes of the present invention, the term "clay minerals" refers to conventional clay minerals or smectites, either natural or synthetic, such as hectorite, fluorohectorite, montomorillonite, nontronite, beidellite, saponite, vermiculite, mica, *etc.*

15 For the purposes of the present invention, the term "crystalline sheet silicates" refers to conventional crystalline sheet silicates, either natural or synthetic, such as kenyaite, magadiite, makatite, kanemite, revdite, grumantite, ilerite, *etc.*

For the purposes of the present invention the term "intercalated catalyst" refers
20 to transition metal which is present within the gallery spaces of a layered inorganic material.

For the purposes of the present invention, the term "intercalated catalyst and support system" refers to the combination of a transition metal catalyst of the present
25 invention and a layered inorganic material of the present invention in which the transition metal catalyst is intercalated into the layered inorganic material. An intercalated catalyst and support system of the present invention may also include other compounds, such as organoaluminum compounds, to aid the catalytic activity of the intercalated catalyst.

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The term “*in situ* transition-metal mediated polymerization” refers to a method for making the exfoliated polymer layered inorganic nanocomposites of the present invention by using transition metal catalysts.

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Description

Polymer layered silicate nanocomposites are novel materials that have improved mechanical, barrier properties, and flammability properties as compared to conventional filled polymer composites. Polymerization of monomer intercalated in gallery space
10 between the plate-like layers of the silicate, *in situ* polymerization, has been used to prepare polymer layered silicate nanocomposites. When *in situ* polymerization occurs in the gallery space, i.e., when the catalyst or reactive site for polymerization resides in the gallery, the system is driven to disperse the layered silicate in the resin by the driving force of the polymerization reaction, see Lan *et al.*, *Mat. Res. Soc. Proc.*, Vol. 435, pp.
15 79-84, (1996) and Fukushima *et al.*, *Clay Minerals*, 23, pp. 27-34, (1988). In instances where the polymerization initiates in the bulk monomer, not in the gallery, no nanocomposite is formed. In addition, the *in situ* polymerization method has been shown to yield polymers with different structures, fewer defects, and better properties. In part, this is due to the confined environment in which the polymer is prepared.
20 Blumstein has shown this in two systems, see Blumstein, “Etude des polymerisations en couche adsorbée I” in *Bull. Chim. Soc.*, pp. 899-905, (1961). Blumstein *et al.*, “Polymerization of Adsorbed Monolayers. II. Thermal Degradation of the Inserted Polymers” in *J. Polymer Sci.*, A3, 2665 (1965). Blumstein found greater thermal stability for polymethylmethacrylate (PMMA) prepared via *in situ* polymerization. The
25 resulting PMMA exhibited better thermal properties, even when separated from the layered silicate host. This effect was attributed to the formation of PMMA with fewer olefinic terminations. Blumstein *et al.* has also demonstrated preparation of poly-2-ethynlpyridine with double the conjugation length, using *in situ* polymerization in a layered silicate, as compared to bulk polymerization, see Blumstein *et al.*, *Polym.*
30 *Preprints*, Vol. 39, No. 2, pp. 701-702, (1998). The commercial polyamide-6 (PA-6) layered silicate nanocomposite has also been prepared via *in situ* polymerization, see

Usuki *et al.*, "Synthesis of nylon 6-clay hybrid" in *J. Mater. Res.* Vol. 8, pp. 1179-1182, (1993). This process forms PA-6 attached, tethered, through PA-6's amine-endgroup to the layered silicate via an ionic interaction to the anionic silica sites. It is proposed that the tether stabilizes the gamma-crystalline form of the PA-6 and prevents growth of large spherulites. The tether has been shown essential for maximum enhancement of thermal and mechanical properties in a variety of systems, see Kojima *et al.*, "Synthesis of nylon t-clay hybrid" in *J. Mater. Res.*, Vol. 8, pp. 1185-1189, (1993) and Giannelis, "Thermal Stability and Mechanical Properties of Vinyl Ester Nanocomposites" in *NIST Grant Quarterly Report*, (1998).

Although melt intercalation has been shown for some systems, this approach has limitations and may not produce the same type of nanocomposites as the *in situ* polymerization approach. Several examples have shown that the driving force of a polymerization reaction is required to obtain complete dispersion of the silicate in the polymer. This *in situ* polymerization method has been proven for polyamides, polyesters and epoxies; however, new methods of preparation are needed, especially for non-polar polymers. The present invention provides novel exfoliated polyolefin layered inorganic nanocomposites prepared using transition metal catalysts, which have been intercalated into the layered inorganic material.

Transition metal catalysts supported on layered silicates have been demonstrated to be useful in U.S. Patent No. 6,048,817 to Sagae *et al.*, the entire contents and disclosure of which is hereby incorporated by reference. However, Sagae *et al.* does not intercalate metallocene or any other catalyst into their layered silicate and only use the catalyst for improved particle size control of the polymer. Also, Sagae *et al.* only used a minute, mass fraction of 0.1 to 0.3%, loading of the metallocene/layered silicate catalysts in the polymerization process, so only a minute amount of layered silicate is present as an impurity in the polymer product.

In contrast, the present invention intercalates a transition metal catalyst, such as a metallocene, into a layered inorganic material, such as layered silicate. Also, the

present invention uses a much higher loading of layered inorganic material. For example, in a polymerization method of the present invention using a metallocene/layered silicate intercalated catalyst and support system, the method of the present invention preferably employs a 3 to 20 times higher loading of layered silicate than Sagae *et al.*, despite employing the same amount of the metallocene. As a result, the layered silicate mass fraction is preferably about 1 to about 20% in a polyolefin material prepared using such an intercalated catalyst and support system. Although metallocene is a preferred intercalated catalyst, chromia and Zigler-Natta intercalated catalysts may also be used. The method of the present invention may be used for *in situ* polymerization of ethylene, propylene, other alpha-olefins, other olefins, and combinations of olefin monomers. Because of the inclusion of the layered inorganic material, the polyolefin materials of the present invention have molecular architectures significantly different from the pure form of the polyolefin.

In the method of the present invention, a transition metal catalyst is intercalated into the gallery spaces of a layered inorganic material to form an intercalated catalyst and support system by conventional methods such as reacting the transition metal catalyst together with the layered inorganic material in a liquid in which the transition metal catalyst is soluble and in which the layered inorganic material forms a suspension. The weight percentage of transition metal catalyst in the intercalated catalyst and support system is generally about 0.01 to 10% by weight, preferably about 0.05 to about 1.0% by weight.

In the method of the present invention an olefin may be polymerized by adding the olefin to be polymerized to the intercalated catalyst and support system. In the case where two olefins are to be copolymerized, one of the olefins may be added to a suspension of the intercalated catalyst and support system in the other olefin. Alternatively, the intercalated catalyst and support system could be added to a solution containing the two monomers to be copolymerized.

In the method of the present invention, the olefin may also be polymerized or a two or more olefins may be copolymerized by a heterogeneous catalytic reaction, by slurry polymerization, or by vapor/gas phase polymerization processes such as those described in U.S. Patent No. 6,048,817 to Sagae *et al.*, the entire contents and disclosure of which is hereby incorporated by reference.

The polymerization of the polyolefin material of the present invention may be carried out in solution, in a slurry, *etc.* and may be carried out at either high or low pressure.

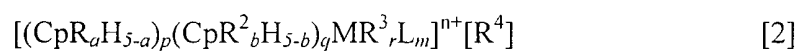
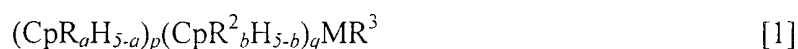
Preferably, the amount of the layered inorganic material present in the form of the intercalated catalyst and support system is sufficient to produce a polyolefin material in which the layered inorganic material comprises at least 1% by weight of the polyolefin material, more preferably about 1 to about 50% by weight of the polyolefin material, and even more preferably about 10 to about 20% by weight of the polyolefin material.

The polyolefin material of the present invention may be formed from any olefin, or mixture of olefins, in the case of a copolymerized polyolefin material. An olefin of the present invention may be cyclic such as norbornylene or polycyclic. Preferred olefins of the present invention include alpha-olefins having 2 to 20 carbon atoms, preferably 2 to 10 carbon atoms. Specific examples of particularly preferred olefins usable in the polymerization method of the present invention include ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-butene, 3-methyl-1-pentene, vinylcycloalkane, ethylenenorbornene derivatives, styrene, and derivatives of the above olefins.

Types of transition metal catalysts that may be used in the method of the present invention include metallocene transition metal compounds, such as the metallocene transition metal compounds described in U.S. Patent No. 6,048,817 to Sagae *et al.*, the entire contents and disclosure of which is hereby incorporated by reference.

Preferred metallocene catalysts include those used in conventional metallocene catalysts for the polymerization of an olefin. For example, a preferred metallocene catalyst may be an organometallic compound comprising an optionally substituted one or two cyclopentadienyl ligands, that is, one or two cyclopentadienyl ring-containing ligand, with substituent being optionally combined to form a condensed ring, and a Group 3, 4, 5, or 6 transition metal of the long form of the Periodic Table, or a cationic complex thereof. The Periodic Table herein means the one based on the 18 Groups recommended by IUPAC in 1989.

Preferred metallocene compounds include compounds represented by the following general formulae [1] and [2]:



In the formulae [1] and [2], Cp represents a conjugated, five-membered ring ligand and R^1 and R^2 represent a substituent on Cp. Therefore, $\text{CpR}_a^1\text{H}_{5-a}$ and $\text{CpR}_b^2\text{H}_{5-b}$ represent derivatives of a cyclopentadienyl (Cp) group.

R^1 and R^2 each independently represent an optionally substituted hydrocarbon group (when substituted, the substituent being preferably, for example, an alkyl group of 1 to 30 carbon atoms, an aryl group of 6 to 30 carbon atoms, or a halogen atom), a silicon-containing group, a phosphorus-containing group, a nitrogen-containing group, and an oxygen-containing group, having 1 to 30 carbon atoms. When a plurality of R^1 s and R^2 s are present, all of R^1 s and R^2 s do not need respectively to represent the same group and R^1 and R^2 may be the same or different.

The examples of R^1 and of R^2 include (i) hydrocarbon groups such as (a) alkyl groups of 1 to 30, preferably 1 to 10 carbon atoms such as methyl, ethyl, propyl,

isopropyl, butyl, isobutyl, t-butyl, pentyl, isopentyl, hexyl, heptyl, octyl, nonyl, and decyl groups, (b) aryl groups of 6 to 30, preferably 6 to 20 carbon atoms such as phenyl, p-tolyl, o-tolyl, and m-tolyl groups, (ii) halo-derivatives of the hydrocarbon group of (i) such as fluoromethyl, fluoroethyl, fluorophenyl, chloromethyl, chloroethyl, chlorophenyl, bromomethyl, bromoethyl, bromophenyl, iodomethyl, iodoethyl, and iodophenyl groups, (iii) silicon-containing hydrocarbon groups of 1 to 30, preferably 1 to 10 carbon atoms such as trimethylsilyl, triethylsilyl, and triphenylsilyl groups, (iv) phosphorus-containing hydrocarbon groups of 1 to 30, preferably 1 to 12 carbon atoms such as dimethylphosphino, diethylphosphino, and diphenylphosphino groups, (v) nitrogen-containing hydrocarbon groups of 1 to 30, preferably 1 to 10 carbon atoms such as dimethylamino, diethylamino, and diisopropylamino groups, (vi) oxygen-containing hydrocarbon groups of 1 to 30, preferably 1 to 20 carbon atoms such as (a) alkoxy groups such as methoxy, ethoxy, and t-butoxy groups, and (b) aryloxy groups such as phenoxy, methylphenoxy, pentamethylphenoxy, p-tolyloxy, m-tolyloxy, and o-tolyloxy groups.

Among these, more preferable R^1 and R^2 , respectively, include alkyl groups of 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and t-butyl groups, alkyl-substituted silicon-containing groups of preferably 1 to 4 carbon atoms in the alkyl such as trimethylsilyl; alkoxy groups of 1 to 4 carbon atoms such as methoxyl group; and aryloxy groups such as phenoxy group.

The two cyclopentadienyl group may or may not be combined through a bridge. The bridge can be construed as consisting of the R^1 and R^2 combined with each other at their ω -terminus when respectively at least one R^1 and R^2 are present on the cyclopentadienyl groups.

Specific examples of the bridge include (i) alkylene groups of 1 to 30, preferably 1 to 20 carbon atoms, for example, methylene and ethylene groups, (ii) alkylidene groups of 1 to 20 carbon atoms, for example, ethylidene and propylidene groups, (iii) silicon-containing bridge groups of 1 to 20 carbon atoms, particularly substituted or

unsubstituted silylene or oligosilylene groups (with the substituent being preferably a lower alkyl group (having 4 or less carbon atoms)), for example, dimethylsilylene, diethylsilylene, diisopropylsilylene, diphenylsilylene, methylethylsilylene, methylphenylsilylene, methylisopropylsilylene and methyl-t-butylsilylene groups, (iv) germanium-containing bridge groups of 1 to 20 carbon atoms, particularly substituted or unsubstituted germylene or oligogermylene groups (wherein the substituent is preferably a lower alkyl group having about four or less carbon atoms), for example, dimethylgermylene, diethylgermylene, dipropylgermylene, diisopropylgermylene, methylethylgermylene, methylphenylgermylene, methylisopropylgermylene and methyl-t-butylgermylene groups, (v) N-containing groups such as amino groups wherein, in the case of secondary or tertiary amino groups, the substituent is preferably a lower alkyl group having four or less carbon atoms, (vi) P-containing groups, such as a phosphinyl group, and (vii) a direct linkage. When two or more of R¹s (or R²s) are present on an identical Cp, the R¹s at their ω -ends (or R²s at their ω -ends) can combine with each other to form a ring.

A specific example thereof is a structure wherein two R¹s, in their ω -ends, bonded respectively to two adjacent carbon atoms in Cp combine with each other to own the two carbon atoms in Cp jointly, thereby forming a condensed ring, typically an indenyl or fluorenyl group. The condensed ring derived from R¹ may be an unsubstituted one (in the case of the above compound, examples of the unsubstituted condensed ring including tetrahydroindenyl and octahydrofluorenyl groups) or a substituted one (examples of preferred substituents including methyl, ethyl, butyl, and phenyl groups). The fact that the condensed ring derived from R¹ is an unsubstituted one means that the total number of carbon atoms of the two R¹s is equal to the number of carbon atoms necessary for the condensed ring. When the total number of carbon atoms of the two R¹s is larger than the number of carbon atoms necessary for the condensed ring, the excess number of carbon atoms serve as a substituent. As with R¹, R² bonded to another Cp in an identical compound can form a condensed ring.

R^3 represents an optionally substituted hydrocarbon group having 1 to 20 carbon atoms (examples of preferred substituents including methyl, ethyl, and benzyl groups), hydrogen, a halogen, a silicon-containing substituent, an alkoxy group, an aryloxy group, an amido group, a thioalkoxy group, $S(O)_s$, R^5 , OR^5 , NR^5 , SiR^5 , or $P(O)_u R^5_3$ wherein s is 0, 1, 2, or 3, t is 0, 1, 2, or 3, u is 0, 1, 2, or 3 and R^5 which may be the same or different represent hydrogen, a halogen, a silicon-containing group, or an optionally halogen-substituted hydrocarbon group having 1 to 20 carbon atoms.

Specific examples of preferred R^3 include (i) alkyl groups, particularly methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, isopentyl, hexyl, heptyl, octyl, nonyl, and decyl groups, (ii) aryl groups, particularly phenyl groups, p-tolyl, o-tolyl, and m-tolyl groups, (iii) halo-substituted hydrocarbon groups, particularly fluoromethyl, fluoroethyl, fluorophenyl, chloromethyl, chloroethyl, chlorophenyl, bromomethyl, bromoethyl, bromophenyl, iodomethyl, iodoethyl, and iodophenyl groups, (iv) halogens, particularly fluorine, chlorine, bromine, and iodine, (v) silicon-containing group, particularly trimethylsilyl, triethylsilyl, and triphenylsilyl groups, (vi) alkoxy, preferably lower alkyloxy groups, particularly methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, and t-butoxy groups, (vii) aryloxy groups, particularly phenoxy, methylphenoxy, pentamethylphenoxy, p-tolyloxy, m-tolyloxy, and o-tolyloxy groups, (viii) amide groups, preferably di-lower-alkyl amido groups, particularly dimethylamido, diethylamido, dipropylamido, diisopropylamido, ethyl-t-butylamido, and bis(trimethylsilyl)amido, (ix) thioalkoxy group, preferably lower alkylthio lower alkyloxy groups, particularly a methylthioalkoxy, ethylthioalkoxy, propylthioalkoxy, butylthioalkoxy, t-butylthioalkoxy, and phenylthioalkoxy groups, and (x) hydrogen. Among them, more preferable are hydrogen, methyl, ethyl, propyl, isopropyl, butyl, phenyl groups, halogen, particularly chloride, methoxy, ethoxy, propoxy, isopropoxy, dimethylamido, and methylthioalkoxy groups; hydrogen, methyl and chlorine being most preferable.

In addition to the above typical examples of R^1 to R^3 , R^3 can combine with R^1 , R^2 , or Cp. Specific examples of preferred ligands include CpH_4 $(CH_2)_n$ O^{--} ($1 \leq n \leq 5$),

CpMe₄ (CH₂)_n O-- (1≤n≤5), CpH₄ (Me₂Si)(t-Bu)N--, and CpMe₄ (Me₂Si)(t-Bu)N-- wherein Cp represents a cyclopentadienyl group, Me represents a methyl group and Bu represents a butyl group. Further, R³s when present in plural can combine with each other to form a bidentate ligand. Specific examples of such R³ include --OCH₂ O--, --
 5 OCH₂ CH₂ O-- and --O(o-C₆ H₄)O--. R¹ to R³ in the nontypical examples of R¹ to R³ are as defined in the case of typical examples so far as there is no contradiction.

M represents a Group 3, 4, 5, or 6 element of the Periodic Table, and specific examples thereof include scandium, yttrium, lanthanum, cerium, praseodymium,
 10 neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, actinium, thorium, protactinium, uranium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten. Among them, titanium, zirconium, and hafnium belonging to the Group 4 of the Periodic Table are preferred. Further, they can be used as a mixture of two or more.

15 L represents an electrically neutral ligand, and m represents an integer of 0 (zero) or more. Specific examples thereof include (i) ethers, especially monoethers, particularly ethers with the hydrocarbon, bonded to ether oxygen, having about 1 to 5 carbon atoms, for example, diethyl ether, tetrahydrofuran, and dioxane, (ii) nitrites,
 20 especially those with the hydrocarbon, bonded to a cyano group, having about 1 to 6 carbon atoms, for example, acetonitrile, (iii) amides, especially N,N-di-lower-alkyl lower fatty acid amides, for example, dimethylformamide, (iv) phosphines, especially tri-lower-alkylphosphines and triphenylphosphine, for example, trimethylphosphine, and (v) amines, especially lower-alkylamines, for example, trimethylamine. Particularly
 25 preferred are tetrahydrofuran, trimethylphosphine, and trimethylamine.

[R⁴] represents an anion for neutralizing a cation, and the number of R⁴s is 1 or not less than 2. Specific examples of [R⁴] include tetraphenyl borate, tetra(p-tolyl) borate, carbadodecaborate, dicarbaundecaborate, tetrakis(pentafluorophenyl) borate,
 30 tetrafluoroborate, hexafluorophosphate. That is, preferred examples of R⁴ include borates containing a hydrocarbon or halohydrocarbon having about 1 to 30 carbon

atoms, or a halogen, and phosphates containing the above groups. Tetraphenyl borate. tetra (p-tolyl) borate, tetrafluoroborate and hexafluorophosphate being preferable.

a and b each independently are an integer of 0 to 5. When the metallocene
 5 compound is represented by the formula [1], p, q, and r are zero or a positive, satisfying $p+q+r=V$ wherein V represents the valency of M, and, when the metallocene compound is represented by the formula [2], p, q, and r are zero or a positive, satisfying $p+q+r=V-n$ wherein V is as defined above. In general, p and q are an integer of 0 to 3, preferably 0 or 1. r is an integer of 0 to 3, preferably 1 or 2. n is an integer satisfying $0 \leq n \leq V$.

10

Specific examples of preferred zirconium compounds in metallocene transition metal compounds represented by the formula [1], among the above metallocene transition metal compounds, include:

- (1) bis(methylcyclopentadienyl)zirconium dichloride,
- 15 (2) bis(ethylcyclopentadienyl)zirconium dichloride,
- (3) bis(methylcyclopentadienyl)zirconium dimethyl,
- (4) bis(ethylcyclopentadienyl)zirconium dimethyl,
- (5) bis(methylcyclopentadienyl)zirconium dihydride,
- (6) bis(ethylcyclopentadienyl)zirconium dihydride,
- 20 (7) bis(dimethylcyclopentadienyl)zirconium dichloride,
- (8) bis(trimethylcyclopentadienyl)zirconium dichloride,
- (9) bis(tetramethylcyclopentadienyl)zirconium dichloride,
- (10) bis(ethyltetramethylcyclopentadienyl)zirconium dichloride,
- (11) bis(indenyl)zirconium dichloride,
- 25 (12) bis(dimethylcyclopentadienyl)zirconium dimethyl,
- (13) bis(trimethylcyclopentadienyl)zirconium dimethyl,
- (14) bis(tetramethylcyclopentadienyl)zirconium dimethyl,
- (15) bis(ethyltetramethylcyclopentadienyl)zirconium dimethyl,
- (16) bis(indenyl)zirconium dimethyl,
- 30 (17) bis(dimethylcyclopentadienyl)zirconium dihydride,
- (18) bis(trimethylcyclopentadienyl)zirconium dihydride,

- (19) bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,
- (20) bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,
- (21) bis(trimethylsilylcyclopentadienyl)zirconium dihydride,
- (22) bis(trifluoromethylcyclopentadienyl)zirconium dichloride,
- 5 (23) bis(trifluoromethylcyclopentadienyl)zirconium dimethyl,
- (24) bis(trifluoromethylcyclopentadienyl)zirconium dihydride,
- (25) isopropylidene-bis(indenyl)zirconium dichloride,
- (26) isopropylidene-bis(indenyl)zirconium dihydride,
- (27) isopropylidene-bis(indenyl)zirconium dihydride,
- 10 (28) pentamethylcyclopentadienyl(cyclopentadienyl)zirconium dichloride,
- (29) pentamethylcyclopentadienyl(cyclopentadienyl)zirconium dimethyl,
- (30) pentamethylcyclopentadienyl(cyclopentadienyl)zirconium dihydride,
- (31) ethyltetramethylcyclopentadienyl(cyclopentadienyl)zirconium dihydride,
- (32) isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
- 15 (33) isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dimethyl,
- (34) dimethylsilyl(cyclopentadienyl)(fluorenyl)-zirconium dimethyl,
- (35) isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dihydride,
- (36) bis(cyclopentadienyl)zirconium dichloride,
- (37) bis(cyclopentadienyl)zirconium dimethyl,
- 20 (38) bis(cyclopentadienyl)zirconium diethyl,
- (39) bis(cyclopentadienyl)zirconium dipropyl,
- (40) bis(cyclopentadienyl)zirconium diphenyl,
- (41) methylcyclopentadienyl(cyclopentadienyl)-zirconium dichloride,
- (42) ethylcyclopentadienyl(cyclopentadienyl)zirconium dichloride,
- 25 (43) methylcyclopentadienyl(cyclopentadienyl)-zirconium dimethyl,
- (44) ethylcyclopentadienyl(cyclopentadienyl)zirconium dimethyl,
- (45) methylcyclopentadienyl(cyclopentadienyl)-zirconium dihydride,
- (46) ethylcyclopentadienyl(cyclopentadiethyl)zirconium dihydride,
- (47) dimethylcyclopentadienyl(cyclopentadienyl)zirconium dichloride,
- 30 (48) trimethylcyclopentadienyl(cyclopentadienyl)zirconium dichloride,
- (49) tetramethylcyclopentadienyl(cyclopentadienyl)zirconium dichloride,

- (50) bis(pentamethylcyclopentadienyl)zirconium dichloride,
(51) tetramethylcyclopentadienyl(cyclopentadienyl)zirconium dichloride,
(52) indenyl(cyclopentadienyl)zirconium dichloride,
(53) dimethylcyclopentadienyl(cyclopentadienyl)zirconium dimethyl,
5 (54) trimethylcyclopentadienyl(cyclopentadienyl)zirconium dimethyl,
(55) tetramethylcyclopentadienyl(cyclopentadienyl)zirconium dimethyl,
(56) bis(pentamethylcyclopentadienyl)zirconium dimethyl,
(57) ethyltetramethylcyclopentadienyl(cyclopentadienyl)zirconium dimethyl,
(58) indenyl(cyclopentadienyl)zirconium dimethyl,
10 (59) dimethylcyclopentadienyl(cyclopentadienyl)zirconium dihydride,
(60) trimethylcyclopentadienyl(cyclopentadienyl)zirconium dihydride,
(61) bis(pentamethylcyclopentadienyl)zirconium dihydride,
(62) indenyl(cyclopentadienyl)zirconium dihydride,
(63) trimethylsilylcyclopentadienyl(cyclopentadienyl)zirconium dimethyl,
15 (64) trimethylsilylcyclopentadienyl(cyclopentadienyl)zirconium dihydride,
(65) trifluoromethylcyclopentadienyl-(cyclopentadienyl)zirconium dichloride,
(66) trifluoromethylcyclopentadienyl-(cyclopentadienyl)zirconium dimethyl,
(67) trifluoromethylcyclopentadienyl-(cyclopentadienyl)zirconium dihydride,
(68) bis(cyclopentadienyl)(trimethylsilyl)(methyl)zirconium,
20 (69) bis(cyclopentadienyl) (triphenylsilyl)(methyl)zirconium,
(70) bis(cyclopentadienyl)[tris(trimethylsilyl)silyl](methyl)zirconium,
(71) bis(cyclopentadienyl)[bis(methylsilyl)silyl](methyl)zirconium,
(72) bis(cyclopentadienyl)(trimethylsilyl)(trimethylsilylmethyl)zirconium,
(73) bis(cyclopentadienyl)(trimethylsilyl)(benzyl)zirconium,
25 (74) methylene-bis(cyclopentadienyl)zirconium dichloride,
(75) ethylene-bis(cyclopentadienyl)zirconium dichloride,
(76) isopropylidene-bis(cyclopentadienyl)zirconium dichloride,
(77) dimethylsilyl-bis(cyclopentadienyl)zirconium dichloride,
(78) methylene-bis(cyclopentadienyl)zirconium dimethyl,
30 (79) ethylene-bis(cyclopentadienyl)zirconium dimethyl,
(80) isopropylidene-bis(cyclopentadienyl)zirconium dimethyl,

- (81) dimethylsilyl-bis(cyclopentadienyl)zirconium dimethyl,
(82) methylene-bis(cyclopentadienyl)zirconium dihydride,
(83) ethylene-bis(cyclopentadienyl)zirconium dihydride,
(84) isopropylidene-bis(cyclopentadienyl)zirconium dihydride,
5 (85) dimethylsilyl-bis(cyclopentadienyl)zirconium dihydride,
(86) bis(cyclopentadienyl)zirconium bis(methanesulfonato),
(87) bis(cyclopentadienyl)zirconium bis(p-toluenesulfonato),
(88) bis(cyclopentadienyl)zirconium bis(trifluoromethanesulfonato)
(89) bis(cyclopentadienyl)zirconium trifluoromethanesulfonato chloride,
10 (90) bis(cyclopentadienyl)zirconium bis(benzenesulfonato),
(91) bis(cyclopentadienyl)zirconium bis(pentafluorobenzenesulfonato),
(92) bis(cyclopentadienyl)zirconium benzenesulfonato chloride,
(93) bis(cyclopentadienyl)zirconium(ethoxy)trifluoromethanesulfonato,
(94) bis(tetramethylcyclopentadienyl)zirconium bis(trifluoromethanesulfonato),
15 (95) bis(indenyl)zirconium bis(trifluoromethanesulfonato),
(96) ethylene-bis(indenyl)zirconium bis(trifluoromethanesulfonato),
(97) isopropylidene-bis(indenyl)zirconium bis(trifluoromethanesulfonato),
(98) (tert-butylamido)dimethyl(tetramethylcyclopentadienyl)silanedibenzylzirconium(tert-butylamido)dimethyl(2,3,4,5-
20 tetramethylcyclopentadienyl)silanedibenzylzirconium,
(99) indenylzirconium tris(dimethylamido),
(100) indenylzirconium tris(diethylamido),
(101) indenylzirconium tris(di-n-propylamido),
(102) cyclopentadienylzirconium tris(dimethylamido),
25 (103) methylcyclopentadienylzirconium tris(dimethylamido),
(104) (tert-butylamido)(tetramethylcyclopentadienyl)-1,2-ethanediylzirconium dichloride,
(105) (methylamido)-(tetramethylcyclopentadienyl)-1,2-ethanediylzirconium dichloride,
(106) (ethylamido)(tetramethylcyclopentadienyl)methylenezirconium chloride,
30 (107) (tert-butylamido)dimethyl(tetramethylcyclopentadienyl)silanezirconium dichloride,

- (108) (benzylamido)dimethyl(tetramethylcyclopentadienyl)silanezirconium dichloride.
 (109) (phenylphosphido)dimethyl(tetramethylcyclopentadienyl)silanezirconium
 dichloride and dibenzyl,
 (110) (benzylamido)dimethyl(tetramethylcyclopentadienyl)silanezirconium dichloride,
 5 (111) (2-methoxyphenylamido)dimethyl(tetramethylcyclopentadienyl)silanezirconium
 dichloride,
 (112) (4-fluorophenylamido)dimethyl(tetramethylcyclopentadienyl)silanezirconium
 dichloride,
 (113) ((2,6-di(1-methylethyl)phenyl)amido)dimethyl
 10 (tetramethylcyclopentadienyl)amidozirconium dichloride,
 (114) bis(1,3-dimethylcyclopentadienyl)zirconium dichloride,
 (115) bis(1-ethyl-3-methylcyclopentadienyl)zirconium dichloride,
 (116) bis(1-n-propyl-3-methylcyclopentadienyl)-zirconium dichloride,
 (117) bis(1-i-propyl-3-methylcyclopentadienyl)zirconium dichloride,
 15 (118) (bis-1-n-butyl-3-methylcyclopentadienyl)-zirconium dichloride,
 (119) bis(1-i-butyl-3-methylcyclopentadienyl)zirconium dichloride,
 (120) bis(1-cyclohexyl-3-methylcyclopentadienyl)zirconium dichloride,
 (121) bis(1,3-dimethylcyclopentadienyl)zirconium dimethyl,
 (122) bis(1-ethyl-3-methylcyclopentadienyl)zirconium dimethyl,
 20 (123) bis(1-n-propyl-3-methylcyclopentadienyl)-zirconium dimethyl,
 (124) bis(1-n-butyl-3-methylcyclopentadienyl)zirconium dimethyl,
 (125) bis(1,3-dimethylcyclopentadienyl)zirconium bis(diethylamido),
 (126) bis(1-ethyl-3-methylcyclopentadienyl)zirconium bis(diethylamido), and
 (127) bis(1-n-butyl-3-methylcyclopentadienyl)zirconium bis(diethylamido).

25

Specific examples of preferred zirconium compounds in metallocene compounds
 represented by the formula [2] include:

- (1) bis(methylcyclopentadienyl)zirconium (chloride) (tetraphenyl borate)tetrahydrofuran
 complex,
 30 (2) bis(ethylcyclopentadienyl)zirconium (chloride) (tetraphenyl borate)tetrahydrofuran
 complex,

- (3) bis(methylcyclopentadienyl)zirconium (methyl) (tetraphenyl borate)tetrahydrofuran complex,
- (4) bis(ethylcyclopentadienyl)zirconium (methyl) (tetraphenyl borate)tetrahydrofuran complex,
- 5 (5) bis(methylcyclopentadienyl)zirconium (hydride) (tetraphenyl borate)tetrahydrofuran complex,
- (6) bis(ethylcyclopentadienyl)zirconium (hydride) (tetraphenyl borate)tetrahydrofuran complex,
- (7) bis(dimethylcyclopentadienyl)zirconium (chloride) (tetraphenyl
- 10 borate)tetrahydrofuran complex,
- (8) bis(trimethylcyclopentadienyl)zirconium (chloride) (tetraphenylborate)tetrahydrofuran complex,
- (9) bis(tetramethylcyclopentadienyl)zirconium (chloride) (tetraphenylborate) tetrahydrofuran complex,
- 15 (10) bis(ethyltetramethylcyclopentadienyl)zirconium (chloride) (tetraphenylborate)tetrahydrofuran complex,
- (11) bis(indenyl)zirconium (chloride) (tetraphenyl borate)tetrahydrofuran complex,
- (12) bis(dimethylcyclopentadienyl)zirconium (methyl) (tetraphenyl borate)tetrahydrofuran complex,
- 20 (13) bis(trimethylcyclopentadienyl)zirconium (methyl) (tetraphenylborate)tetrahydrofuran complex,
- (14) bis(tetramethylcyclopentadienyl)zirconium (methyl) (tetraphenylborate)tetrahydrofuran complex,
- (15) bis(ethyltetramethylcyclopentadienyl)zirconium (methyl) (tetraphenylborate)tetrahydrofuran complex,
- 25 (16) bis(indenyl)zirconium (methyl) (tetraphenylborate)tetrahydrofuran complex,
- (17) bis(dimethylcyclopentadienyl)zirconium (hydride) (tetraphenylborate)tetrahydrofuran complex,
- (18) bis(trimethylcyclopentadienyl)zirconium (hydride) (tetraphenyl
- 30 borate)tetrahydrofuran complex,

- (19) bis(ethyltetramethylcyclopentadienyl)zirconium (hydride)
(tetraphenylborate)tetrahydrofuran complex,
- (20) bis(trimethylsilylcyclopentadienyl)zirconium (methyl)
(tetraphenylborate)tetrahydrofuran complex,
- 5 (21) bis(trimethylsilylcyclopentadienyl)zirconium (hydride)
(tetraphenylborate)tetrahydrofuran complex,
- (22) bis(trifluoromethylcyclopentadienyl)zirconium (methyl)
(tetraphenylborate)tetrahydrofuran complex,
- (23) bis(trifluoromethylcyclopentadienyl)zirconium (hydride)
- 10 (tetraphenylborate)tetrahydrofuran complex,
- (24) isopropylidene-bis(indenyl)zirconium (chloride) (tetraphenyl
borate)tetrahydrofuran complex,
- (25) isopropylidene-bis(indenyl)zirconium (methyl) (tetraphenyl borate)tetrahydrofuran
complex,
- 15 (26) isopropylidene-bis(indenyl)zirconium (hydride) (tetraphenyl borate)tetrahydrofuran
complex,
- (27) pentamethylcyclopentadienyl(cyclopentadienyl)zirconium (chloride) (tetraphenyl
borate)tetrahydrofuran complex,
- (28) ethyltetramethylcyclopentadienyl(cyclopentadienyl)zirconium (chloride)
- 20 (tetraphenylborate)tetrahydrofuran complex,
- (29) pentamethylcyclopentadienyl (cyclopentadienyl)zirconium (methyl)
(tetraphenylborate)tetrahydrofuran complex,
- (30) ethyltetramethylcyclopentadienyl(cyclopentadienyl)zirconium (methyl)
(tetraphenylborate)tetrahydrofuran complex,
- 25 (31) pentamethylcyclopentadienyl)zirconium (hydride)
(tetraphenylborate)tetrahydrofuran complex,
- (32) ethyltetramethylcyclopentadienyl)zirconium (hydride)
(tetraphenylborate)tetrahydrofuran complex,
- (33) isopropylidene(cyclopentadienyl)(fluorenyl)zirconium (chloride) (tetraphenyl
- 30 borate)tetrahydrofuran complex,

- (34) isopropylidene (cyclopentadienyl)(fluorenyl)zirconium (methyl)
(tetraphenylborate)tetrahydrofuran complex,
- (35) isopropylidene (cyclopentadienyl)(fluorenyl)zirconium (hydride)
(tetraphenylborate)tetrahydrofuran complex,
- 5 (36) bis(cyclopentadienyl)zirconium (chloride) (tetraphenylborate)tetrahydrofuran
complex,
- (37) bis(cyclopentadienyl)(methyl)zirconium (tetraphenyl borate)tetrahydrofuran
complex,
- (38) bis(cyclopentadienyl)(ethyl)zirconium (tetraphenylborate)tetrahydrofuran complex.
- 10 (39) bis(cyclopentadienyl)(propyl)zirconium (tetraphenylborate)tetrahydrofuran
complex,
- (40) bis(cyclopentadienyl)(phenyl)zirconium (tetraphenylborate)tetrahydrofuran
complex,
- (41) methylcyclopentadienyl(cyclopentadienyl)zirconium (chloride) (tetraphenyl
15 borate)tetrahydrofuran complex,
- (42) ethylcyclopentadienyl(cyclopentadienyl)zirconium (chloride)
(tetraphenylborate)tetrahydrofuran complex,
- (43) bis(ethylcyclopentadienyl)zirconium (chloride) (tetraphenylborate)tetrahydrofuran
complex,
- 20 (44) methylcyclopentadienyl (cyclopentadienyl)zirconium (methyl) (tetraphenylborate)-
tetrahydrofuran complex.
- (45) ethylcyclopentadienyl (cyclopentadienyl)zirconium (methyl) (tetraphenylborate)-
tetrahydrofuran complex,
- (46) methylcyclopentadienyl (cyclopentadienyl)zirconium (hydride) (tetraphenylborate)-
25 tetrahydrofuran complex,
- (47) ethylcyclopentadienyl (cyclopentadienyl)zirconium (hydride) (tetraphenylborate)-
tetrahydrofuran complex,
- (48) dimethylcyclopentadienyl(cyclopentadienyl)zirconium (chloride) (tetraphenyl
borate)tetrahydrofuran complex,
- 30 (49) trimethylcyclopentadienyl (cyclopentadienyl)zirconium (chloride)
(tetraphenylborate)-tetrahydrofuran complex,

- (50) tetramethylcyclopentadienyl (cyclopentadienyl)zirconium (chloride) (tetraphenylborate)-tetrahydrofuran complex,
- (51) bis(pentamethylcyclopentadienyl)zirconium (chloride) (tetraphenylborate)tetrahydrofuran complex,
- 5 (52) indenyl(cyclopentadienyl)zirconium (chloride) (tetraphenyl borate)tetrahydrofuran complex,
- (53) dimethylcyclopentadienyl (cyclopentadienyl)zirconium (methyl) (tetraphenylborate)-tetrahydrofuran complex,
- (54) trimethylcyclopentadienyl(cyclopentadienyl)zirconium (methyl) (tetraphenyl
- 10 borate)tetrahydrofuran complex,
- (55) tetramethylcyclopentadienyl (cyclopentadienyl)zirconium (methyl) (tetraphenylborate)-tetrahydrofuran complex,
- (56) bis(pentamethylcyclopentadienyl)zirconium (methyl) (tetraphenylborate)tetrahydrofuran complex,
- 15 (57) cyclopentadienyl (indenyl)zirconium (methyl) (tetraphenylborate)tetrahydrofuran complex,
- (58) dimethylcyclopentadienyl (cyclopentadienyl)zirconium (hydride) (tetraphenylborate)tetrahydrofuran complex,
- (59) trimethylcyclopentadienyl (cyclopentadienyl)zirconium (hydride)
- 20 (tetraphenylborate)-tetrahydrofuran complex,
- (60) bis(pentamethylcyclopentadienyl)zirconium (hydride) (tetraphenylborate)-tetrahydrofuran complex,
- (61) indenyl(cyclopentadienyl)zirconium (hydride) (tetraphenylborate) tetrahydrofuran complex,
- 25 (62) trimethylsilylcyclopentadienyl(cyclopentadienyl)zirconium (methyl) (tetraphenylborate) tetrahydrofuran complex,
- (63) trimethylsilylcyclopentadienyl(cyclopentadienyl)zirconium (hydride) (tetraphenylborate)tetrahydrofuran complex,
- (64) trifluoromethylcyclopentadienyl(cyclopentadienyl)zirconium (hydride)
- 30 (tetraphenylborate)tetrahydrofuran complex,

- (65) bis(cyclopentadienyl)(trimethylsilyl)zirconium (tetraphenyl borate)tetrahydrofuran complex,
- (66) bis(cyclopentadienyl) (triphenylsilyl)zirconium (tetraphenylborate)tetrahydrofuran complex,
- 5 (67) bis(cyclopentadienyl)[tris(trimethylsilyl)silyl]-zirconium (tetraphenylborate)tetrahydrofuran complex,
- (68) bis(cyclopentadienyl)(trimethylsilylmethyl)zirconium (tetraphenyl borate)tetrahydrofuran complex,
- (69) bis(cyclopentadienyl) (benzyl)zirconium (tetraphenylborate)tetrahydrofuran
- 10 complex,
- (70) methylene-bis(cyclopentadienyl)zirconium (chloride) (tetraphenylborate)tetrahydrofuran complex,
- (71) ethylene-bis(cyclopentadienyl)zirconium (chloride) (tetraphenyl borate)tetrahydrofuran complex,
- 15 (72) isopropylidene-bis(cyclopentadienyl)zirconium (chloride) (tetraphenylborate)tetrahydrofuran complex,
- (73) dimethylsilyl-bis(cyclopentadienyl)zirconium (chloride) (tetraphenyl borate)tetrahydrofuran complex,
- (74) methylene-bis(cyclopentadienyl)zirconium (methyl)
- 20 (tetraphenylborate)tetrahydrofuran complex,
- (75) ethylene-bis(cyclopentadienyl)zirconium (methyl) (tetraphenyl borate)tetrahydrofuran complex,
- (76) isopropylidene-bis(cyclopentadienyl)zirconium (methyl) (tetraphenylborate)tetrahydrofuran complex,
- 25 (77) dimethylsilyl-bis(cyclopentadienyl)zirconium (methyl) (tetraphenyl borate)tetrahydrofuran complex,
- (78) methylene-bis(cyclopentadienyl)zirconium (hydride) (tetraphenylborate)tetrahydrofuran complex,
- (79) ethylene-bis(cyclopentadienyl)zirconium (hydride) (tetraphenyl
- 30 borate)tetrahydrofuran complex,
- (80) isopropylidene-bis(cyclopentadienyl)zirconium (hydride)

- (tetraphenylborate)tetrahydrofuran complex,
 (81) dimethylsilyl-bis(cyclopentadienyl)zirconium (hydride)
 (tetraphenylborate)tetrahydrofuran complex,
 (82) bis(cyclopentadienyl)zirconium (methanesulfonato) (tetraphenyl
 5 borate)tetrahydrofuran complex,
 (83) bis(cyclopentadienyl)zirconium (p-toluenesulfonato)
 (tetraphenylborate)tetrahydrofuran complex,
 (84) bis(cyclopentadienyl)zirconium (trifluoromethanesulfonato)
 (tetraphenylborate)tetrahydrofuran complex,
 10 (85) bis(cyclopentadienyl)zirconium (benzenesulfonato)
 (tetraphenylborate)tetrahydrofuran complex,
 (86) bis(cyclopentadienyl)zirconium (pentafluorobenzenesulfonato) (tetraphenylborate)-
 tetrahydrofuran complex,
 (87) bis(tetramethylcyclopentadienyl)zirconium (trifluoromethanesulfonato)
 15 (tetraphenylborate)-tetrahydrofuran complex,
 (88) bis(indenyl)zirconium (trifluoromethanesulfonato)
 (tetraphenylborate)tetrahydrofuran complex,
 (89) ethylenebis(indenyl)zirconium (trifluoromethanesulfonato) (tetraphenylborate)-
 tetrahydrofuran complex, and
 20 (90) isopropylidene-bis(indenyl)zirconium (trifluoromethanesulfonato)
 (tetraphenylborate)-tetrahydrofuran complex.

Examples of the Group 3, 4, 5, and 6 metal compounds, for example, titanium
 compounds, hafnium compounds and the like, include similar compounds as described
 25 above. It is needless to say that a mixture of compounds belonging to the same group
 and/or a mixture of compounds belonging to different groups may also be used.

The layered inorganic material of the present invention may be any suitable
 layered inorganic material that may have a transition metal catalyst intercalate within the
 30 layered inorganic material. Preferred layered inorganic materials of the present invention
 include layered metal oxides, particularly layered silicates, and most preferably 2:1

layered silicates. Silicates useful as the layered inorganic material of the present invention include, polysilicic acids, crystalline sheet silicates, clay minerals (smectite or smectite clays), synthetic smectite derivatives, mixed layered clays, synthetic mixed layered clays, vermiculites, hydromicas, micas, synthetic mica-like derivatives and mixtures thereof. Preferred clay minerals include montmorillonite, hectorite, saponite, nontronite, beidellite, fluorohectorite, and laponite, and mixed layered silicates such as rectorite, synthetic mica montmorillonite, and illite and vermiculite and mica-like compositions such as muscovite, biotite, phlogopite, synthetic mica montmorillonite, taeniolite, and tetrasilicic mica. Other preferred layered inorganic materials of the present invention include layered phosphates, arsenates, titanates, molybdates, niobates, vanadates, and manganates. Suitable layered silicates, phosphates, arsenates, titanates and niobates useful as the layered inorganic material of the present invention are described in U.S. Patent No. 5,853,886 to Pinnavaia, *et al.*, the entire contents and disclosure of which is hereby incorporated by reference. Suitable layered silicates for the layered inorganic material of the present invention are also described in U.S. Patent No. 5,747,560 to Christiani, *et al.*, and in U.S. Patent No. 5,773,502 to Takekoshi, *et al.*, the entire contents and disclosures of which are hereby incorporated by reference. Other suitable layered inorganic materials include layered fluoromica compounds such as the layered fluoromica compounds described in U.S. Patent No. 5,414,042 to Yasue, *et al.*, the entire contents and disclosure of which is hereby incorporated by reference. Other suitable layered inorganic materials are described in U.S. Patent No. 5,530,052 to Takekoshi, *et al.*, the entire contents and disclosure of which is incorporated herein by reference.

Preferably, the layered inorganic material of the present invention is at least 0.1 nm thick and has a minimum width of 10 nm or larger.

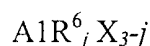
In order to make the layered inorganic material of the present invention more compatible with the polymer to be formed by the method of the present invention, the layered inorganic material may be treated with a polymer compatibilizing agent. Suitable compounds for use as compatibilizing agents and method for treating the

layered inorganic material of the present invention with a compatibilizing agent are described in U.S. Patent No. 5,747,560 to Christiani, *et al.*, the entire contents and disclosure of which is hereby incorporated by reference. Other suitable compatibilizing agents include onium compounds, such as the onium compounds described in U.S. Patent Nos. 5,773,502 and 5,530,052 to Takekoshi, *et al.*, and the ammonium salts, pyridinium salts, sulfonium salts and phosphonium salts of U.S. Patent No. 5,102,948 to Deguchi, *et al.*, the entire contents and disclosures of which are hereby incorporated by reference.

10 In general, an intercalated catalyst and support system of the present invention comprising a transition metal catalyst and a layered inorganic material has sufficient catalytic activity for the polymerization of an olefin. If necessary, however, an organoaluminum compound may be further used in combination with the transition metal catalyst and the layered inorganic material in the transition metal catalyst of the present invention. The addition of an organoaluminum compound to the intercalated catalyst and support system of the present invention may provide a better catalyst for the polymerization of an olefin, particularly when the transition metal catalyst is a metallocene catalyst.

20 It is believed that the organoaluminum compound used in the polymerization method of the present invention inhibits a lowering in catalytic activity caused by water and the like present in the polymerization system and at the same time contributes to an improvement in catalytic activity. Therefore, addition of the organoaluminum compound is one of the preferred embodiments of the present invention.

25 Organoaluminum compounds usable in the present invention include, for example, those represented by the following formula:



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wherein R^6 represents a hydrocarbon group having 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms; X represents hydrogen, a halogen, or an alkoxy group; and j is a number represented by $0 < j \leq 3$. Preferred are trialkylaluminums, for example, trimethylaluminum, triethylaluminum, tripropylaluminum, trisobutylaluminum, tri-n-butylaluminum and tri-n-hexylaluminum; alkylaluminum hydride, for example, diethylaluminum hydride, and diisobutylaluminum hydride; halogen- or alkoxy-containing alkylaluminums, for example, diethylaluminum monochloride and diisobutylaluminum monochloride, and diethylaluminum methoxide diisobutylaluminum methoxide; and alkylaluminum amides, for example, diethylaluminum (diethylamide), and diisobutylaluminum (diethylamide). In addition to the above organoaluminum compounds, aluminoxanes, such as methylaluminoxane, can be used. Among them, trialkylaluminums such as triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, and tri-n-hexylaluminum are particularly preferred.

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The reaction between the olefin monomer with the intercalated catalyst and support system may be carried out in an inert gas, such as nitrogen gas, or an inert hydrocarbon solvent, such as pentane, hexane, heptane, toluene, or xylene. The contact temperature is preferably between -20°C . and the boiling point of the solvent, particularly preferably between room temperature and the boiling point of the solvent.

20

The polyolefin material of the present invention included at least 1% of a layered inorganic material. As a result of the inclusion of this much layered inorganic material, the polyolefin material of the present invention may have properties that are significantly different from polyolefin that constitutes part of the polyolefin material. For example, the inclusion of the layered inorganic material may result in the polyolefin material having a tensile strength of at least 125%, perhaps 200% or more of the tensile strength of the polyolefin in a pure form. The polyolefin material of the present invention may also have a tensile modulus of at least 125% of the tensile modulus, perhaps 200% or more, of the tensile modulus of the polyolefin in a pure form. The

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polyolefin material may have a UV stability of at least 125% of the UV stability, perhaps 200% or more, of the UV stability of the polyolefin in a pure form.

5 The polyolefin material of the present invention may have an elongation of at least 67% of the elongation of the polyolefin in a pure form. The polyolefin material of the present invention may have also an impact strength of at least 67% of the impact strength of the polyolefin in a pure form. In addition, the polyolefin material of the present invention may have a flammability of no more than 67% of the flammability of the polyolefin in a pure form. Also, the polyolefin material of the present invention may
10 have a permeability of no more than 67% of the permeability of the polyolefin in a pure form.

The present invention will now be described by way of example:

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EXAMPLE 1

Reaction of Montmorillonite K10 with $(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ru}(\text{CHC}_6\text{H}_5)$

In a 100 mL round bottom flask, 5.36 g of montmorillonite 0.13 g (0.16 mmol) of $(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ru}(\text{CHC}_6\text{H}_5)$, a Ru transition metal catalyst, were dry mixed for 15 minutes to form a montmorillonite supported Ru catalyst, followed by rapid addition of
20 30 mL of CH_2Cl_2 to form a suspension. The suspension was stirred for one hour, filtered, and the filtercake washed with CH_2Cl_2 (3 x 10 mL) to yield a colorless filtrate. The filtrate was dried in vacuo for 8 hours at 0.1 Torr and weighed (5.32 g, 99.2% yield, 2.4 wt. % Ru catalyst). X-ray analysis showed a peak in the low angle region at 8.8° two theta, indicative of a layer separation of 0.99 nanometers.

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EXAMPLE 2

In a 100 mL round bottom flask 2.60 g (0.028 mmol) of norbornylene was dissolved in CH_2Cl_2 and cooled to -19°C . The cooled norbornylene solution was added rapidly to a 100 mL round bottom flask containing 0.23 g of the montmorillonite
30 supported ruthenium catalyst of Example 1 suspended in CH_2Cl_2 (25 mL, -19°C). Upon mixing, the polymerization of norbornylene was observed to occur, resulting in an

increased viscosity of the solution was observed to occur, resulting in an increased viscosity of the solution. The reaction was allowed to stir for 12 hours, was filtered, and was suspended in 200 mL CHCl_3 and precipitated by addition to a flask containing 400 mL of methanol. The isolated rubber sold was weighed (2.21 g, 78.1% yield). X-ray
5 analysis showed no peak in the low angle region (1 to 10° two theta), indicative of formation of a polynorbornylene-montmorillonite nanocomposite.

EXAMPLE 3

10 Ruthenium catalysts were intercalated into layered silicates for preparation of nanocomposites via ring opening metathesis polymerization. The transition metal catalysts were selected because of their chemical stability and solubility in polar protic solvents and water. Specifically, the ruthenium carbene catalysts, recently reported, see
15 Mohr, *et al.*, *Organometallics*, Vol. 15, pp. 4317-4325 (1996), the entire contents and disclosure of which is hereby incorporated by reference, with phosphine ligands bearing quaternary alkylammonium groups are employed. This approach has produced polynorbornylene layered silicate nanocomposites. The nanostructure is characterized
20 by the loss of the d_{001} peak (at $2\text{-theta} = 7.5^\circ$) from the sodium montmorillonite in the low angle region of the x-ray powder diffraction.

EXAMPLE 4

Olefins are polymerized using an intercalated catalyst and support system comprising chromium trioxide intercalated into a layered silicate. The intercalated
25 catalyst and support system is prepared as described in European Patent EP 683180 A2. the entire contents and disclosure of which is hereby incorporated by reference.

EXAMPLE 5

30 Olefins are polymerized using an intercalated catalyst and support system comprising a metallocene intercalated into a layered silicate. The intercalated catalyst

and support system is prepared as described in U.S. Patent No. 5,853,886 to Pinnavaia, *et al.* and in U.S. Patent No. 6,048,817 to Sagae *et al.* the entire contents and disclosure of which are hereby incorporated by reference.

5 Although the present invention has been fully described in conjunction with the preferred embodiment thereof with reference to the accompanying drawings, it is to be understood that various changes and modifications may be apparent to those skilled in the art. Such changes and modifications are to be understood as included within the scope of the present invention as defined by the appended claims, unless they depart
10 therefrom.

WHAT IS CLAIMED IS:

1. A method for forming a polyolefin material comprising:
providing at least one olefin monomer; and
polymerizing said olefin monomer using an intercalated catalyst and support system to form a polyolefin material comprising a polyolefin and a layered inorganic material wherein said intercalated catalyst and support system comprises a sufficient amount of said layered inorganic material so that said layered inorganic material comprises at least 1% by weight of said polyolefin material.
2. The method of claim 1, wherein said layered inorganic material comprises about 1 to about 50% by weight of said polyolefin material.
3. The method of claim 1, wherein said layered inorganic material comprises about 10 to about 20% by weight of said polyolefin material.
4. The method of claim 1, wherein a transition metal catalyst comprises about 0.01 to about 10% by weight of said intercalated catalyst and support system.
5. The method of claim 1, wherein a transition metal catalyst comprises about 0.05 to about 1.0% by weight of said intercalated catalyst and support system.
6. The method of claim 1, wherein said polyolefin comprise polyethylene.
7. The method of claim 1, wherein said polyolefin comprises polypropylene.
8. The method of claim 1, wherein said polyolefin material comprises about 10 to about 20% by weight of said layered inorganic material.
9. The method of claim 1, wherein said layered inorganic material comprises a layered silicate.

10. The method of claim 1, wherein said layered inorganic material comprises montmorillonite.
11. The method of claim 1, wherein said intercalated catalyst and support system comprises a metallocene transition metal catalyst.
12. The method of claim 1, further comprising treating said layered inorganic material with a compatibilizing agent.
13. The method of claim 1, wherein said intercalated catalyst and support system further comprises an organoaluminum compound.
14. The method of claim 1, wherein said layered inorganic material is selected from the group of layered inorganic materials consisting of: clay minerals, polysilicic acids, crystalline sheet silicates, and layered phosphates, arsenates, titanates, molybdates, niobates, vanadates, and manganates.
15. A polyolefin material comprising:
 - a polyolefin; and
 - a layered inorganic material, said layered inorganic material comprising at least 1% by weight of said polyolefin material.
16. The polyolefin material of claim 15, wherein said layered inorganic material comprises about 1 to about 50% by weight of said polyolefin material.
17. The polyolefin material of claim 15, wherein said layered inorganic material comprises about 10 to about 20% by weight of said polyolefin material.
18. The polyolefin material of claim 15, wherein said polyolefin comprise polyethylene.

19. The polyolefin material of claim 15, wherein said polyolefin comprises polypropylene.
20. The polyolefin material of claim 15, wherein said layered inorganic material comprises a layered silicate.
21. The polyolefin material of claim 15, wherein said layered inorganic material comprises montmorillonite.
22. The polyolefin material of claim 15, wherein said polyolefin material has a tensile strength of at least 125% of the tensile strength of said polyolefin in a pure form.
23. The polyolefin material of claim 15, wherein said polyolefin material has a tensile strength of at least 200% of the tensile strength of said polyolefin in a pure form.
24. The polyolefin material of claim 15, wherein said polyolefin material has a tensile modulus of at least 125% of the tensile modulus of said polyolefin in a pure form.
25. The polyolefin material of claim 15, wherein said polyolefin material has a tensile modulus of at least 200% of the tensile modulus of said polyolefin in a pure form.
26. The polyolefin material of claim 15, wherein said polyolefin material has a UV stability of at least 125% of the UV stability of said polyolefin in a pure form.
27. The polyolefin material of claim 15, wherein said polyolefin material has a UV stability of at least 200% of the UV stability of said polyolefin in a pure form.
28. The polyolefin material of claim 15, wherein said polyolefin material has an elongation of at least 67% of the elongation of said polyolefin in a pure form.

29. The polyolefin material of claim 15, wherein said polyolefin material has at least 67% of the impact strength of said polyolefin in a pure form.
30. The polyolefin material of claim 15, wherein said polyolefin material has a flammability of no more than 67% of the flammability of said polyolefin in a pure form.
31. The polyolefin material of claim 15, wherein said polyolefin material has a permeability of no more than 67% of the permeability of said polyolefin in a pure form.