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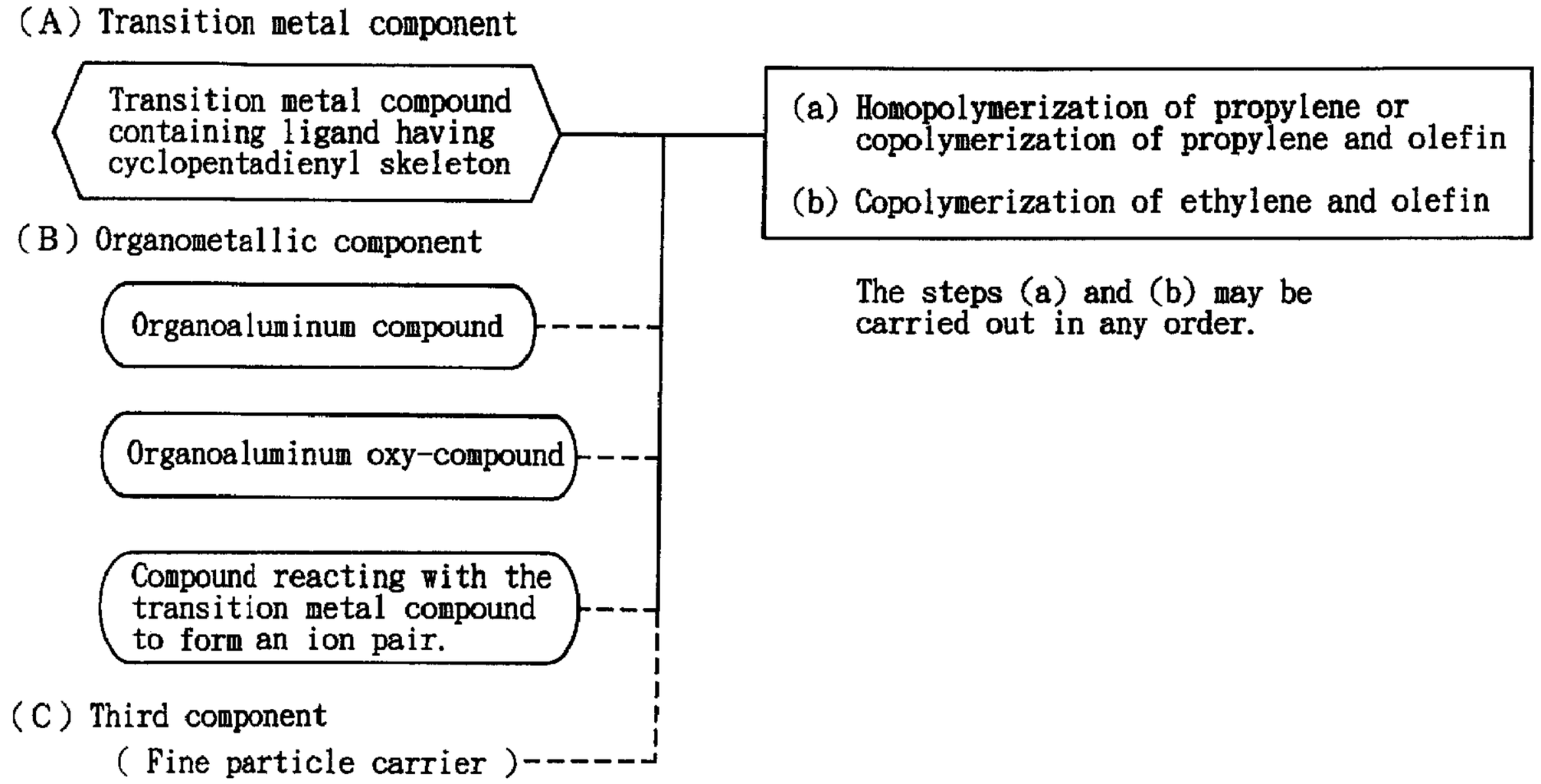
(54) Titre : PROCEDE DE PRODUCTION D'UNE COMPOSITION DE POLYMERE DE PROPYLENE, ET COMPOSITION DE POLYMERE DE PROPYLENE

(54) Title: PROCESS FOR PREPARING PROPYLENE POLYMER COMPOSITION, AND PROPYLENE POLYMER COMPOSITION



(57) Abrégé/Abstract:
A process for preparing a propylene polymer composition comprising conducting multistage polymerization including a step (a) for preparing a propylene (co)polymer (a) and a step (b) for preparing an ethylene copolymer (b) in the presence of (A) a transition metal compound and (B) a compound activating the transition metal compound (A), in which the steps (a) and (b) may be carried out in any order, and the resulting propylene polymer composition contains the propylene (co)polymer (a) in an amount of 20 to 90 % by weight and the ethylene copolymer (b) in an amount of 10 to 80 % by weight and has MFR, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 500 g/10 min; and a propylene polymer composition prepared by this process. The process according to the invention can prepare a propylene polymer composition having excellent rigidity, heat resistance and impact resistance.

ABSTRACT

A process for preparing a propylene polymer composition comprising conducting multistage polymerization including a step (a) for preparing a propylene (co)polymer (a) and a step (b) for preparing an ethylene copolymer (b) in the presence of (A) a transition metal compound and (B) a compound activating the transition metal compound (A), in which the steps (a) and (b) may be carried out in any order, and the resulting propylene polymer composition contains the propylene (co)polymer (a) in an amount of 20 to 90 % by weight and the ethylene copolymer (b) in an amount of 10 to 80 % by weight and has MFR, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 500 g/10 min; and a propylene polymer composition prepared by this process.

The process according to the invention can prepare a propylene polymer composition having excellent rigidity, heat resistance and impact resistance.

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TITLE

PROCESS FOR PREPARING PROPYLENE POLYMER COMPOSITION

AND PROPYLENE POLYMER COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a process for preparing a propylene polymer composition, and a propylene polymer composition prepared by the process, more particularly to a process for preparing a propylene polymer composition using multistage polymerization and a propylene polymer composition prepared by such process.

BACKGROUND OF THE INVENTION

Because of their excellent rigidity, heat resistance and impact resistance, propylene polymers are used for various molded articles in many fields.

For further improving the impact resistance of propylene polymers, there is known a process comprising initially homopolymerizing propylene and then copolymerizing propylene and ethylene to prepare a block copolymer.

For example, Japanese Patent Laid-Open Publication No. 337308/1992 discloses a process for preparing a block copolymer in which propylene is first homopolymerized or copolymerized with ethylene in the presence of a transition

metal compound having as a ligand a cyclopentadienyl bridged with a silylene group and an organoaluminum compound so as to produce a propylene homopolymer or a propylene copolymer containing less than 6 % by weight of ethylene, in an amount of 40 to 95 % by weight based on the total weight of the final polymer product; and then ethylene and propylene in a weight ratio of 10/10 to 95/5 are further copolymerized in the presence of the same transition metal compound and the same organoaluminum compound until a copolymer is produced in an amount of 60 to 5 % by weight based on the total weight of the final polymer product. This publication also describes that the block copolymer obtained by this process has well balanced properties between impact resistance and rigidity.

Japanese Patent Laid-Open Publication No. 202152/1993 discloses a process for preparing a polypropylene molding material comprising (1) 20 to 99 % by weight of a crystalline polymer having a propylene unit content of not less than 95 % by weight and (2) 1 to 80 % by weight of a non-crystalline ethylene-propylene copolymer having an ethylene unit content of 20 to 90 % by weight, in the presence of a catalyst comprising a transition metal compound and an organoaluminum compound, in which polymerization to prepare the non-crystalline ethylene-propylene copolymer is carried out using a specific bridged metallocene compound and aluminoxane. This publication also describes that the polypropylene molding material

obtained by this process has excellent properties, particularly in low-temperature impact strength.

However, there has recently been an increasingly severe demand for properties of polypropylene compositions. In addition, there has also been a need for a propylene polymer composition having well balanced properties among rigidity, heat resistance and impact resistance, and a process capable of preparing such composition.

DESCRIPTION OF THE INVENTION

The process for preparing a propylene polymer composition according to the invention comprises:

conducting multistage polymerization including the following steps (a) and (b) in the presence of

(A) a transition metal compound containing a ligand having a cyclopentadienyl skeleton and

(B) a compound activating the transition metal compound (A),

in which the steps (a) and (b) may be carried out in any order, and the second stage polymerization is carried out in the presence of a polymer obtained by the first stage polymerization to produce a propylene polymer composition comprising 20 to 90 % by weight of a propylene (co)polymer (a) obtained in the step (a) and 10 to 80 % by weight of an ethylene copolymer (b) obtained in the step

(b), the composition having a melt flow rate, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 500 g/10 min;

the step (a):

(i) homopolymerizing propylene or (ii) copolymerizing propylene and at least one olefin selected from ethylene and olefins of 4 to 20 carbon atoms to prepare a propylene (co)polymer (a) comprising not less than 80 mol % of constituent units derived from propylene, the propylene (co)polymer (a) having a melting point, as measured by a differential scanning calorimeter, of not lower than 100 °C and a melt flow rate, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 1,000 g/10 min;

the step (b):

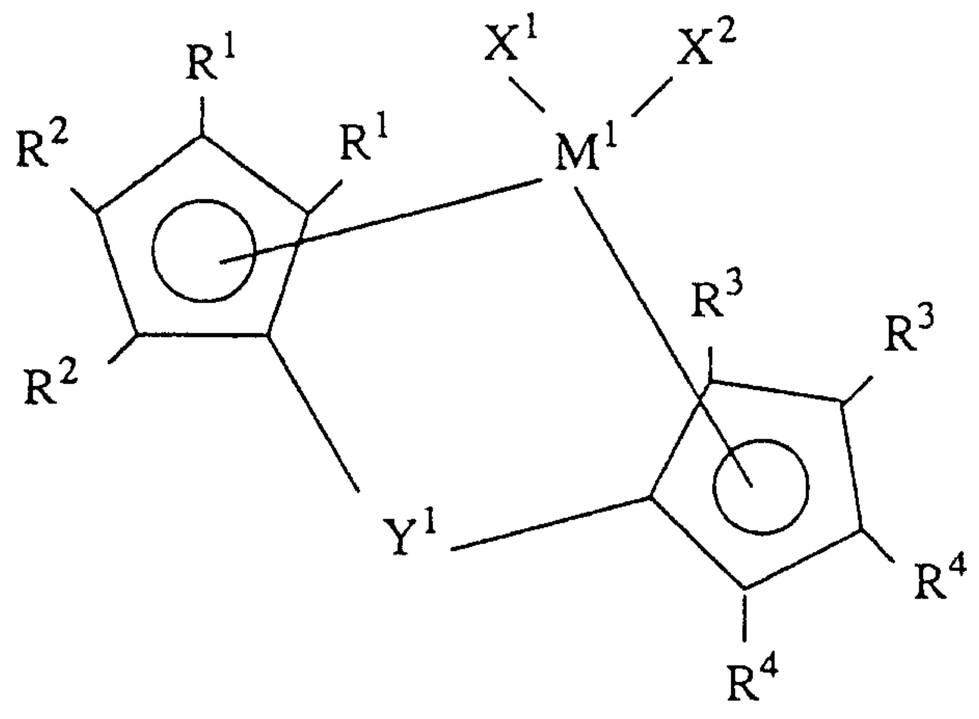
copolymerizing ethylene and at least one olefin selected from olefins of 4 to 20 carbon atoms to prepare an ethylene copolymer (b) comprising more than 50 mol % of constituent units derived from ethylene, the ethylene copolymer (b) having an intrinsic viscosity [η], as measured in decalin at 135 °C, of 0.1 to 20 dl/g.

In the present invention, preferably the ethylene copolymer (b) prepared in the step (b) has an intrinsic viscosity [η], as measured in decalin at 135°C, of 0.1 to 20 dl/g, a density of 0.85 to 0.91 g/cm^3, an Mn/Mw value indicating a molecular weight distribution of 1.4 to 3.5, and a melt flow rate of 0.1 to 45 g/10 min.

According to the invention, preferably the multistage polymerization is carried out in the order of the step (a) and then the step (b).

Further, it is preferred that propylene is homopolymerized in the step (a) and ethylene and 1-butene are copolymerized in the step (b).

In the present invention, as the transition metal compound containing a ligand having a cyclopentadienyl skeleton is preferably used a compound represented by the following formula (II), more preferably a compound represented by the following formula (III):



(II)

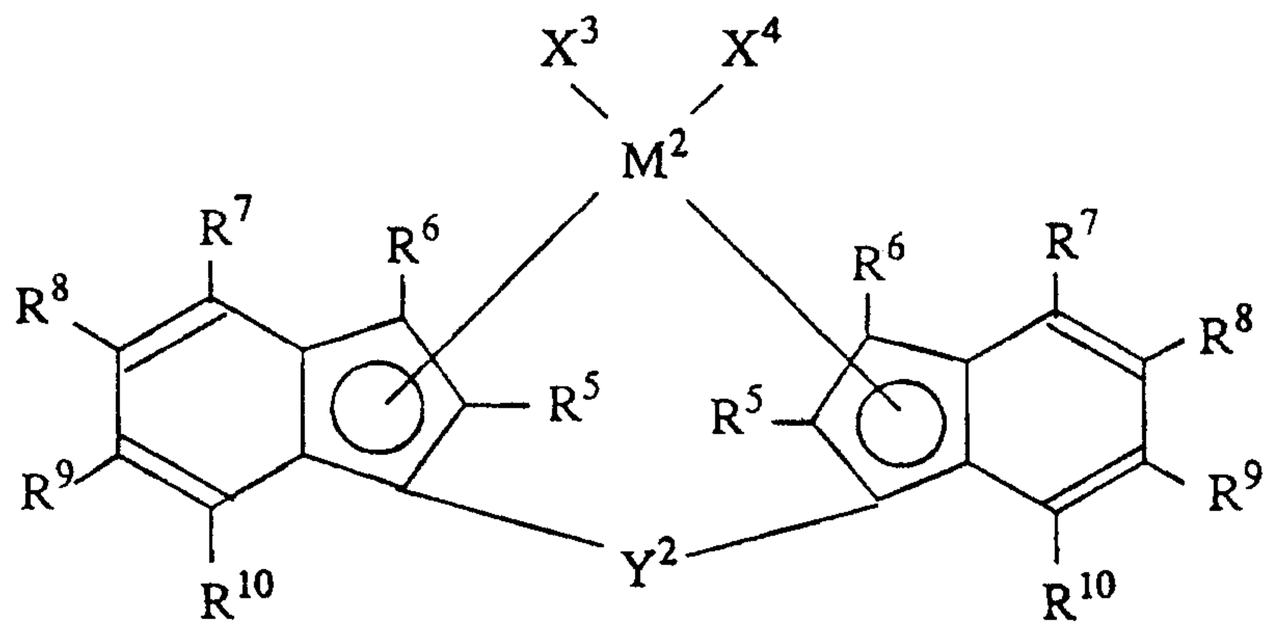
wherein M^1 is a transition metal atom of Group IVB to Group VIB of the periodic table;

R^1, R^2, R^3 and R^4 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group, and a part of adjacent groups R^1, R^2, R^3 and R^4 may be bonded to form together with the carbon atoms to which they are attached a ring, wherein R^1

to R^4 at two positions, for example even R^1 and R^1, may be the same or different, and R having the same suffix show a preferable combination for linking to form a ring;

Y^1 is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group; and

X^1 and X^2 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group or a sulfur-containing group;



(III)

wherein M^2 is a transition metal atom of group IVB to Group VIB of the periodic table;

R^5, R^6 and R^8 to R^{10}, which may be the same or different, are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group;

R^7 is an aryl group of 6 to 16 carbon atoms;

Y^2 is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group; and

X^3 and X^4 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group or a sulfur-containing group.

In the present invention, as the compound (B) activating the transition metal compound (A) is preferably used at least one compound selected from the group consisting of, for example,

(B-1) an organoaluminum compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair.

According to the process of the invention, a propylene polymer composition having well balanced properties among rigidity, heat resistance and impact resistance can be obtained.

The propylene polymer composition according to the present invention is prepared by the process of the invention as described above.

The propylene polymer composition of the invention has well balanced properties among rigidity, heat resistance and impact resistance.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is an explanatory view showing steps for preparing an olefin polymerization catalyst used in the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The process for preparing a propylene polymer composition according to the invention, and such a composition obatined will be described in detail hereinafter.

The term "polymerization" used herein is intended to mean both "homopolymerization" and "copolymerization". Also, the term "polymer" used herein is intended to mean both "homopolymer" and "copolymer".

In the process for preparing a propylene polymer composition according to the invention, the propylene (co)polymer (a) and the ethylene copolymer (b) are prepared in the presence of:

(A) a transition metal compound containing a ligand having a cyclopentadienyl skeleton, and

(B) a compound activating the transition metal compound (A).

First, the transition metal compound (A) containing a ligand having a cyclopentadienyl skeleton and the compound

(B) activating the transition metal compound (A) are described.

The transition metal compound (A) containing a ligand having a cyclopentadienyl skeleton may be specifically a transition metal compound represented by the formula (I):

$$ML_x \qquad (I)$$

wherein M is a transition metal of Group IVB to Group VIB of the periodic table, for example, zirconium (Zr), titanium (Ti), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo) and tungsten (W); x is a valence of the transition metal; and

L is a ligand coordinated to the transition metal, and at least one of L is a ligand having a cyclopentadienyl skeleton, preferably at least two of L are ligands having a cyclopentadienyl skeleton.

The ligand having a cyclopentadienyl skeleton may be condensed with a benzene ring, a naphthalene ring, an acenaphthene ring, an indene ring, to form a further ring.

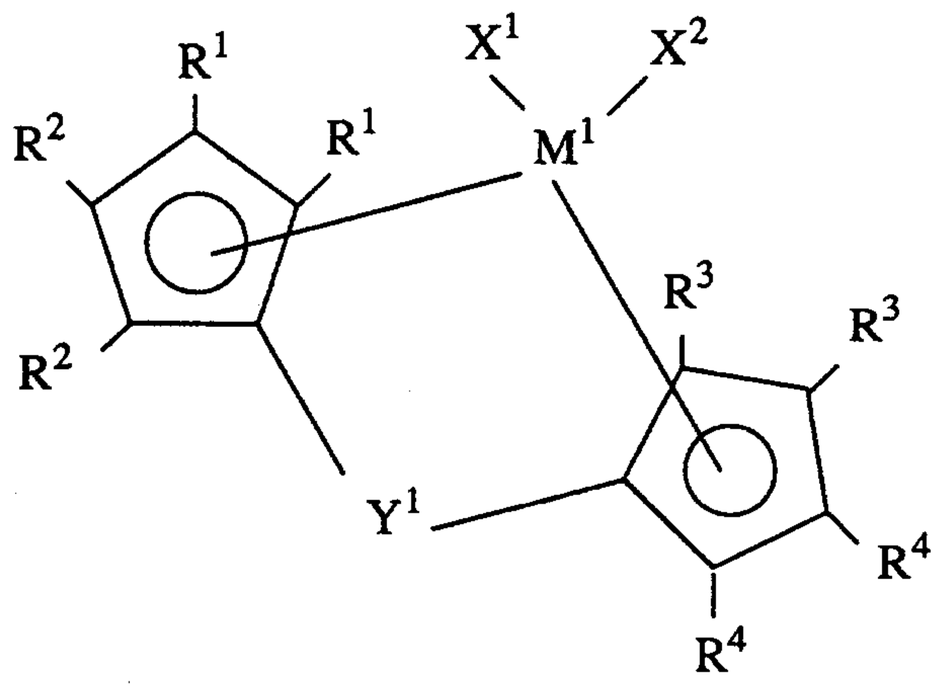
Examples of the ligands having a cyclopentadienyl skeleton include cyclopentadienyl group, indenyl group, 4,5,6,7-tetrahydroindenyl group, 4,5,6,6a-tetrahydropentalenyl group, 7,8-dihydro-3H,6H-as-indacenyl group and fluorenyl group. These groups may be substituted with a halogen, a hydrocarbon group, a halogenated hydrocarbon group, a silicon-containing group, an oxygen-

containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group.

When the transition metal compound of the formula (I) contains two or more of groups having a cyclopentadienyl skelton, two of them are preferably linked through a hydrocarbon group, a halogenated hydrocarbon group, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group.

L other than the ligand having a cyclopentadienyl skeleton is a hydrogen, a halogen, a hydrocarbon group, a halogenated hydrocarbon group, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group.

The transition metal compound (A) used in the invention is preferably a compound represented by the following formula (II), more preferably a compound represented by the following formula (III).



(II)

In this formula, M^1 is the same transition metal as defined for M in the formula (I), and preferably is titanium, zirconium or hafnium.

R^1, R^2, R^3 and R^4 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group, and a part of adjacent groups R^1, R^2, R^3 and R^4 may be bonded to each other to form together with the carbon atoms to which they are bonded a ring. R^1 to R^4 each at two positions, respectively, for example, even R^1 and R^1, may be the same or different, and R having the same suffix show a preferable combination for linking to form a ring.

Examples of the halogens include fluorine, chlorine, bromine and iodine.

Examples of the hydrocarbon groups of 1 to 20 carbon atoms include alkyl groups, such as methyl, ethyl, propyl, butyl, hexyl, cyclohexyl, octyl, nonyl, dodecyl, eicosyl, norbornyl and adamantyl; alkenyl groups, such as vinyl, propenyl and cyclohexenyl; arylalkyl groups, such as benzyl, phenylethyl and phenylpropyl; and aryl groups, such as phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl, biphenyl, naphthyl, methylnaphthyl, anthracenyl and phenanthryl.

Examples of rings formed by bonding these hydrocarbon groups include condensed ring groups such as benzene ring,

naphthalene ring, acenaphthene ring and indene ring; and these condensed ring groups where one or more hydrogen atoms on the ring are replaced with alkyl groups such as methyl, ethyl, propyl and butyl.

Examples of the halogenated hydrocarbon groups include those hydrocarbon groups as mentioned above which are substituted by a halogen.

Examples of the silicon-containing groups include monohydrocarbon-substituted silyls, such as methylsilyl and phenylsilyl; dihydrocarbon-substituted silyls, such as dimethylsilyl and diphenylsilyl; trihydrocarbon-substituted silyls, such as trimethylsilyl, triethylsilyl, tripropylsilyl, tricyclohexylsilyl, triphenylsilyl, dimethylphenylsilyl, methyldiphenylsilyl, tritolylsilyl and trinaphthylsilyl;

silyl ethers of hydrocarbon-substituted silyls, such as trimethylsilyl ether;

silicon-substituted alkyl groups, such as trimethylsilylmethyl; and silicon-substituted aryl groups, such as trimethylphenyl.

Examples of the oxygen-containing groups include hydroxyl group; alkoxy groups, such as methoxy, ethoxy, propox and butoxy; aryloxy groups, such as phenoxy, methylphenoxy, dimethylphenoxy and naphthoxy; and arylalkoxy groups, such as phenylmethoxy and phenylethoxy.

Examples of the sulfur-containing groups include those where the oxygen in the oxygen-containing groups as mentioned above is replaced with sulfer.

Examples of the nitrogen-containing groups include amino group; alkylamino groups, such as methylamino, dimethylamino, diethylamino, dipropylamino, dibutylamino and dicyclohexylamino; and arylamino groups and alkylarylamino groups, such as phenylamino, diphenylamino, ditolylamino, dinaphthylamino and methylphenylamino.

Examples of the phosphorus-containing groups include phosphino groups, such as dimethylphosphino and diphenylphosphino.

Of these, preferred are hydrocarbon groups. Particularly preferred are hydrocarbon groups of 1 to 4 carbon groups such as methyl, ethyl, propyl and butyl; benzene rings formed by bonding hydrocarbon groups; and these condensed benzene rings where one or more hydrogen atoms on the ring are substituted by alkyl groups such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl and tert-butyl.

Y^1 is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group.

More specifically, there can be mentioned:

divalent hydrocarbon groups of 1 to 20 carbon atoms, for example, alkylene groups such as methylene, dimethylmethylene, 1,2-ethylene, dimethyl-1,2-ethylene, 1,3-trimethylene, 1,4-tetramethylene, 1,2-cyclohexylene and 1,4-cyclohexylen, and arylalkylene groups such as diphenylmethylene and diphenyl-1,2-ethylene;

divalent halogenated hydrocarbon groups, for example, those divalent hydrocarbon groups of 1 to 20 carbon atoms as mentioned above which are halogenated, such as chloromethylene;

divalent silicon-containing groups, for example, arylsilylene groups such as methylsilylene, dimethylsilylene, diethylsilylene, di(n-propyl)silylene, di(i-propyl)silylene, di(cyclohexyl)silylene, methylphenylsilylene, diphenylsilylene, di(p-tolyl)silylene and di(p-chlorophenyl)silylene, and alkyldisilyl, alkylaryldisilyl and aryldisilyl groups such as tetramethyl-1,2-disilyl and tetraphenyl-1,2-disilyl; and

divalent germanium-containing groups, for example, those divalent silicon-containing groups as mentioned above where the silicon is replaced with germanium.

Of these, preferred are substituted silylene groups, such as dimethylsilylene, diphenylsilylene and methylphenylsilylene.

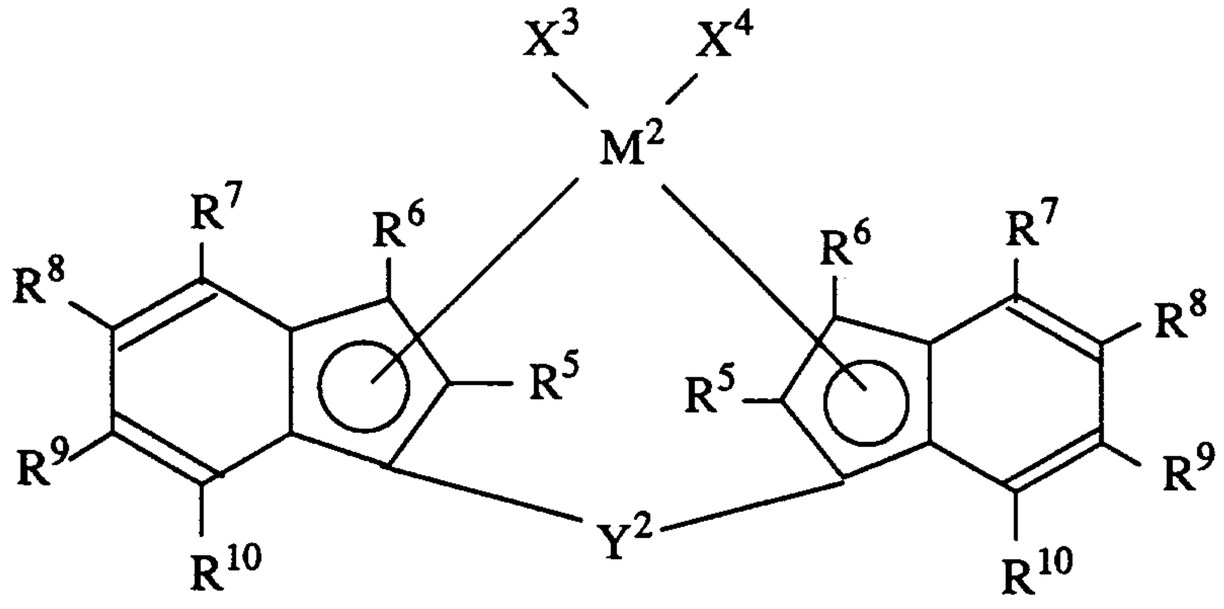
X^1 and X^2 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group or a sulfur-containing group.

Specifically, there can be mentioned the same halogens, hydrocarbon groups of 1 to 20 carbon atoms, halogenated hydrocarbon groups of 1 to 20 carbon atoms and oxygen-containing groups as described for R^1, R^2, R^3 and R^4. Examples of the sulfur-containing groups include the same sulfur-containing groups as described for R^1, R^2, R^3 and R^4;

and further, sulfonato groups such as methylsulfonato, trifluoromethanesulfonato, phenylsulfonato, benzylsulfonato, p-toluenesulfonato, trimethylbenzenesulfonato, triisobutylbenzenesulfonato, p-chlorobenzenesulfonato and pentafluorobenzenesulfonato; and sulfinato groups such as methylsulfinato, phenylsulfinato, benzenesulfinato, p-toluenesulfinato, trimethylbenzenesulfinato and pentafluorobenzenesulfinato.

Of these, preferred are halogens, hydrocarbon groups of 1 to 20 carbon atoms and sulfonato groups.

Particularly preferably used as the transition metal compound (A) in the invention is a compound represented by the following formula (III).



(III)

In this formula, M^2 is a transition metal atom as described for M in the formula (I), and preferably is titanium, zirconium or hafnium, and particularly zirconium.

R^5, R^6 and R^8 to R^{10}, which may be the same or different, are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, a silicon-containing group,

an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group as described for R^1, R^2, R^3 and R^4 in the formula (II).

R^7 is an aryl group of 6 to 16 carbon atoms, for example, phenyl, α-naphthyl, β-naphthyl, anthracenyl, phenanthryl, pyrenyl, acenaphthyl, phenalenyl or aceanthrylenyl. Of these, preferred is phenyl, naphthyl or phenanthryl. These aryl groups may be substituted with halogens, hydrocarbon groups of 1 to 20 carbon atoms and halogenated hydrocarbon groups of 1 to 20 carbon atoms as described for R^1, R^2, R^3 and R^4 in the formula (II).

Y^2 is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group as described for Y^1 in the formula (II).

X^3 and X^4 are each hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group or a sulfur-containing group as described for X^1 and X^2 in the formula (II).

Listed below are examples of the transition metal compounds (A) containing a ligand having a cyclopentadienyl skeleton, usable in the invention.

Bis(cyclopentadienyl)zirconium dichloride,

Bis(indenyl)zirconium dichloride,

Bis(fluorenyl)zirconium dichloride,

Bis(n-propylcyclopentadienyl)zirconium dichloride,

Bis(t-butylcylopentadienyl)zirconium dichloride,

Bis(trimethylsilylcyclopentadienyl)zirconium dichloride,

Bis(neopentylcyclopentadienyl)zirconium dichloride,

rac-Ethylene-bis(1-indenyl)zirconium dichloride,

rac-Ethylene-bis(1-indenyl)zirconium dibromide,

rac-Ethylene-bis(1-indenyl)dimethylzirconium,

rac-Ethylene-bis(1-indenyl)diphenylzirconium,

rac-Ethylene-bis(1-indenyl)methylzirconium monochloride,

rac-Ethylene-bis(1-indenyl)zirconiumbis(methanesulfonato),

rac-Ethylene-bis(1-indenyl)zirconiumbis(p-toluenesolfonate),

rac-Ethylene-bis(1-indenyl)zirconiumbis(trifluoromethanesulfonato),

rac-Ethylene-bis{1-(4,5,6,7-tetrahydroindenyl)}zirconium dichloride,

Isopropylidene{1-cyclopentadienyl-1-(3-methylcyclopentadienyl)}zirconium dichloride,

Isopropylidene{1-(3-t-butylcyclopentadienyl)-1-(3-t-butylindenyl)}zirconium dichloride,

Isopropylidene(1-cyclopentadienyl-9-fluorenyl)zirconium dichloride,

Isopropylidene{1-cyclopentadienyl-9-(2,7-di(t-butyl)fluorenyl)}zirconium dichloride,

Isopropylidene{1-(3-methylcyclopentadienyl)-9-fluorenyl}zirconium dichloride,

rac-Dimethylsilylene-bis(1-cyclopentadienyl)zirconium dichloride,

rac-Dimethylsilylene-bis{1-(3-methylcyclopentadienyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2,4-dimethylcyclopentadienyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2,3,5-trimethylcyclopentadienyl)}zirconium dichloride,

rac-Dimethylsilylene-bis(1-indenyl)zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-i-propylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,

rac-Diphenyllsilylene-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4,6-(di-i-propyl)indenyl}zirconium dichloride,

Dimethylsilylene-bis(1-cyclopentadienyl-1-indenyl)zirconium dichloride,

rac-Dimethylsilylene-bis(1,2-dihydroacenaphthylo[4,5-b]cyclopentadienyl)zirconium dichloride,

rac-Dimethylsilylene-bis(benzo[e]indenyl)zirconium dichloride,

rac-Dimethylsilylene-bis{1-(4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(α-naphthyl)indenyl}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(β-naphthyl)indenyl}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(1-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(2-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(9-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-fluorophenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(pentafluorophenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-chlorophenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(m-chlorophenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(o-chlorophenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(o,p-dichlorophenyl)phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-bromophenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-tolyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(m-tolyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(o-tolyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(o,o'-dimethylphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-ethylphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-i-propylphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-benzylphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-biphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(m-biphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(p-trimethylsilylphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-(m-trimethylsilylphenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-ethyl-4-(α-naphthyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-ethyl-4-(β-naphthyl)indenyl}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-ethyl-4-(1-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-ethyl-4-(2-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-ethyl-4-(9-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-ethyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,

rac-Diphenylsilylene-bis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-phenyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-n-propyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-n-propyl-4-(α-naphthyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-n-propyl-4-(β-naphthyl)indenyl}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-n-propyl-4-(1-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-n-propyl-4-(2-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-n-propyl-4-(9-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-n-propyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-i-butyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-i-butyl-4-(α-naphthyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-i-butyl-4-(β-naphthyl)indenyl}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-i-butyl-4-(1-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-i-butyl-4-(2-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-i-butyl-4-(9-anthracenyl)indenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-i-butyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,

rac-Diethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Di-(i-propyl)silylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Di-(n-butyl)silylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Dicyclohexylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Methylphenylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Diphenylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Di(p-tolyl)silylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Di(p-chlorophenyl)silylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Methylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Ethylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylgermylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dibromide,

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium dimethyl,

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium methylchloride,

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium chloride SO_2Me,

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}zirconium chloride OSO_2Me,

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}titanium dichloride, and

rac-Dimethylsilylene-bis{1-(2-methyl-4-phenylindenyl)}hafnium dichloride.

Also employable are transition metal compounds corresponding to the above mentioned compounds where the metal zirconium, titanium or hafnium is replaced with a metal vanadium, niobium, tantalum, chromium, molybdenum or tungsten.

The compound (B) which activates the transition metal compound (A) (hereinafter sometimes referred to as "activating compound"), that is used in the process for preparing a propylene polymer composition according to the invention, may be selected from the group consisting of:

(B-1) an organoaluminum compound [component (B-1)],

(B-2) an organoaluminum oxy-compound [component (B-2)], and

(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair [component (B-3)].

As the activating compound (B), two or more components selected from the components (B-1) to (B-3) can be used in combination, and a preferred combination is the component (B-1) and the component (B-2).

The organoaluminum compound (B-1) used for preparing a propylene polymer composition together with the transition metal compound (A) is, for example, an organoaluminum compound represented by the formula (IV):

$$R^a_nAlX_{3-n} \qquad (IV)$$

wherein R^a is a hydrocarbon group of 1 to 12 carbon atoms, X is a halogen atom or a hydrogen atom, and n is 1 to 3.

In the formula (IV), R^a is a hydrocarbon group of 1 to 12 carbon atoms, for example, an alkyl group, a cycloalkyl group or an aryl group, including for example methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, cyclopentyl, cyclohexyl, phenyl and tolyl.

Specifically, such organoaluminum compound (B-1) may be as follows:

trialkylaluminums, such as trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, trioctylaluminum, tri(2-ethylhexyl)aluminum and tridecylaluminum;

alkenylaluminums, such as isoprenylaluminum;

dialkylaluminum halides, such as dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, diisobutylaluminum chloride and dimethylaluminum bromide;

alkylaluminum sesquihalides, such as methylaluminum sesquichoride, ethylaluminum sesquichloride, isopropylaluminum sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide;

alkylaluminum dihalides, such as methylaluminum dichloride, ethylaluminum dichloride, isopropylaluminum dichloride and ethylaluminum dibromide; and

alkylaluminum hydrides, such as diethylaluminum hydride and diisobutylaluminum hydride.

Also employable as the organoaluminum compound (B-1) is a compound represented by the formula (V):

$$R^a_nAlY_{3-n} \qquad (V)$$

wherein R^a is the same as defined above; Y is $-OR^b$ group, $-OSiR^c_3$ group, $-OAlR^d_2$ group, $-NR^e_2$ group, $-SiR^f_3$ group or $-N(R^g)AlR^h_2$ group; n is 1 to 2; R^b, R^c, R^d and R^h are each

methyl, ethyl, isopropyl, isobutyl, cyclohexyl, phenyl or the like, R^e is hydrogen, methyl, ethyl, isopropyl, phenyl, trimethylsilyl or the like; and R^f and R^g are each methyl, ethyl or the like.

Examples of such organoaluminum compounds include:

(1) compounds of the formula $R^a_nAl(OR^b)_{3-n}$, e.g., dimethylaluminum methoxide, diethylaluminum ethoxide and diisobutylaluminum methoxide;

(2) compounds of the formula $R^a_nAl(OSiR^c_3)_{3-n}$, e.g., $Et_2Al(OSiMe_3)$, $(iso\text{-}Bu)_2Al(OSiMe_3)$ and $(iso\text{-}Bu)_2Al(OSiEt_3)$;

(3) compounds of the formula $R^a_nAl(OAlR^d_2)_{3-n}$, e.g., $Et_2AlOAlEt_2$ and $(iso\text{-}Bu)_2AlOAl(iso\text{-}Bu)_2$;

(4) compounds of the formula $R^a_nAl(NR^e_2)_{3-n}$, e.g., Me_2AlNEt_2, $Et_2AlNHMe$, $Me_2AlNHEt$, $Et_2AlN(SiMe_3)_2$ and $(iso\text{-}Bu)_2alN(SiMe_3)_2$;

(5) compounds of the formula $R^a_nAl(SiR^f_2)_{3-n}$, e.g., $(iso\text{-}Bu)_2AlSiMe_3$; and

(6) compounds of the formula $R^a_nAl(N(R^g)AlR^h_2)_{3-n}$, e.g., $Et_2AlN(Me)AlEt_2$ and $(iso\text{-}Bu)_2AlN(Et)Al(iso\text{-}Bu)_2$.

Of the organoaluminum compounds represented by the formula (IV) or (V), preferred are compounds of the formula R^a_3Al, and particularly preferred are compounds of the same formula wherein R^h is an isoalkyl group.

Such organoaluminum compounds (B-1) can be used singly or in combination of two or more kinds.

The organoaluminum oxy-compound (B-2) used for preparing a propylene polymer composition together with the transition metal compound (A) may be either aluminoxane

conventionally known or such a benzene-insoluble organoaluminum oxy-compound as exemplified in Japanese Patent Laid-Open Publication No. 78687/1990.

The conventionally known aluminoxane can be prepared by, for example, the following procedures.

(1) A procedure of adding an organoaluminum compound such as trialkylaluminum to a hydrocarbon medium suspension of compounds containing adsorbed water or salts containing water of crystallization, e.g., magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate and cerous chloride hydrate, so as to allow the organoaluminum compound to react with the adsorbed water or the water of crystallization.

(2) A procedure of allowing water, ice or water vapor to directly act on an organoaluminum compound such as trialkylaluminum in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

(3) A procedure of allowing organotin oxide such as dimethyltin oxide or dibutyltin oxide to react with an organoaluminum compound such as trialkylaluminum in a medium such as decane, benzene or toluene.

The aluminoxane may contain a small amount of an organometallic component. Further, it is possible that the solvent or the unreacted organoaluminum compound is distilled off from the solution recovered and the residue is dissolved again in a solvent or suspended in a poor solvent for aluminoxane.

Examples of the organoaluminum compounds used for preparing aluminoxane include:

trialkylaluminums, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum and tridecylaluminum;

tricycloalkylaluminums, such as tricyclohexylaluminum and tricyclooctylaluminum;

dialkylaluminum halides, such as dimethylaluminum chloride, diethylaluminum chloride, diethylaluminum bromide and diisobutylaluminum chloride;

dialkylaluminum hydrides, such as diethylaluminum hydride and diisobutylaluminum hydride;

dialkylaluminum alkoxides, such as dimethylaluminum methoxide and diethylaluminum ethoxide; and

dialkylaluminum aryloxide, such as diethylaluminum phenoxide.

Of these, preferred are trialkylaluminums and tricycloalkylaluminums, and particularly preferred is trimethylaluminum.

Also employable as the organoaluminum compound used for preparing aluminoxane is isoprenylaluminum represented by the formula (VI):

$$(iC_4H_9)_xAl_y(C_5H_{10})_z \qquad \text{(VI)}$$

wherein x, y and z are each a positive number, and $z \geq 2x$.

The organoaluminum compounds mentioned above are used singly or in combination.

Examples of the solvents used for preparing aluminoxane include aromatic hydrocarbons, such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons, such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions, such as gasoline, kerosine and gas oil; and halides of these aromatic, aliphatic and alicyclic hydrocarbons, particularly chlorides and bromides thereof. In addition, ethers such as ethyl ether and tetrahydrofuran can be also employed. Of the solvents, preferred are aromatic hydrocarbons and aliphatic hydrocarbons.

Such organoaluminum oxy-compounds (B-2) as mentioned above can be used singly or in combination of two or more kinds.

The compound (B-3) which reacts with the transition metal compound (A) to form an ion pair, that is used for preparing a propylene polymer composition together with the transition metal compound (A), includes Lewis acid, ionic compounds and carborane compounds, as described for example in WO88/05792 (published August 11, 1988) and WO88/05793 (published July 13, 1989), Japanese Patent Laid-Open Publication No. 179005/1991, No. 179006/1991, No.

207703/1991 and No. 207704/1991, and U.S. Patent No. 547,718.

The Lewis acid includes magnesium-containing Lewis acid, aluminum-containing Lewis acid and boron-containing Lewis acid. Of these, boron-containing Lewis acid is preferred.

The Lewis acid which contains a boron atom is, for example, a compound represented by the formula:

$$BR^iR^jR^k \qquad \text{(VII)}$$

wherein R^i, R^j and R^k are each independently a phenyl group which may have substituents such as fluorine, methyl and trifluoromethyl, or a fluorine atom.

Examples of the compounds represented by the above formula (VII) include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron. Of these, particularly preferred is tris(pentafluorophenyl)boron.

The ionic compound employable in the invention is a salt comprising a cationic compound and an anionic compound. The anion reacts with the transition metal compound (A) to render the compound (A) cationic and to form an ion pair, resulting in stabilizing the transition metal cation species. Examples of such anion include organoboron compound anion, organoarsenic compound anion

and organoaluminum compound anion. Preferred are those relatively bulky and stabilizing the transition metal cation species. Examples of cation include metallic cation, organometallic cation, carbonium cation, tripium cation, oxonium cation, sulfonium cation, phosphonium cation and ammonium cation. More specifically, there can be mentioned triphenylcarbenium cation, tributylammonium cation, N,N-dimethylammonium cation, ferrocenium cation, etc.

Of these, preferred are ionic compounds containing a boron compound as anion, and examples thereof include:

trialkyl-substituted ammonium salts, such as triethylammoniumtetra(phenyl)boron, tripropylammoniumtetra(phenyl)boron, tri(n-butyl)ammoniumtetra(phenyl)boron, trimethylammoniumtetra(p-tolyl)boron, trimethylammoniumtetra(o-tolyl)boron, tributylammoniumtetra(pentafluorophenyl)boron, tripropylammoniumtetra(o,p-dimethylphenyl)boron, tributylammoniumtetra(m,m-dimethylphenyl)boron, tributylammoniumtetra(p-trifluoromethylphenyl)boron, tri(n-butyl)ammoniumtetra(o-tolyl)boron and tri(n-butyl)ammoniumtetra(4-fluorophenyl)boron;

N,N,-dialkylanilinium salts, such as N,N-dimethylaniliniumtetra(phenyl)boron, N,N-diethylaniliniumtetra(phenyl)boron and N,N-2,4,6-pentamethylaniliniumtetra(phenyl)boron;

dialkylammonium salts, such as di(n-propyl)ammoniumtetra(pentafluorophenyl)boron and dicyclohexylammoniumtetra(phenyl)boron; and

triarylphosphonium salts, such as triphenylphosphoniumtetra(phenyl)boron, tri(methylphenyl)phosphoniumtetra(phenyl)boron and tri(dimethylphenyl)phosphoniumtetra(phenyl)boron.

Also employable as the ionic compound which contains a boron atom are triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate and ferroceniumtetrakis(pentafluorophenyl)borate.

Further, the following compounds can be also employed. (In the ionic compounds listed below, the counter ion is tri(n-butyl)ammonium, but not intended to limit thereto.)

Salts of anions, for example, bis[tri(n-butyl)ammonium]nonaborate, bis[tri(n-butyl)ammonium]decaborate, bis[tri(n-butyl)ammonium]undecaborate, bis[tri(n-butyl)ammonium]dodecaborate, bis[tri(n-butyl)ammonium]decachlorodecaborate, bis[tri(n-butyl)ammonium]dodecachlorododecaborate, tri(n-butyl)ammonium-1-carbadecaborate, tri(n-butyl)ammonium-1-carbaundecaborate, tri(n-butyl)ammonium-1-carbadodecaborate, tri(n-butyl)ammonium-1-trimethylsilyl-1-carbadecaborate and tri(n-butyl)ammoniumbromo-1-carbadodecaborate.

Moreover, borane compounds and carborane compounds can be also employed. These compounds are employed as the Lewis acid or the ionic compounds.

Examples of the borane and carborane compounds include:

borane and carborane complex compounds and salts of carborane anions, such as, decaborane(14), 7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13), undecahydride-7,8-dimethyl-7,8-dicarbaundecaborane, dodecahydride-11-methyl-2,7-dicarbaundecaborane, tri(n-butyl)ammonium-6-carbadecaborate(14), tri(n-butyl)ammonium-6-carbadecaborate(12), tri(n-butyl)ammonium-7-carbaundecaborate(13), tri(n-butyl)ammonium-7,8-dicarbaundecaborate(12), tri(n-butyl)ammonium-2,9-dicarbaundecaborate(12), tri(n-butyl)ammoniumdodecahydride-8-methyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-ethyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-butyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-allyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-9-trimethylsilyl-7,8-dicarbaundecaborate and tri(n-butyl)ammoniumundecahydride-4,6-dibromo-7-carbaundecaborate; and

carboranes and salts of carboranes, such as, 4-carbanonaborane(14), 1,3-dicarbanonaborane(13), 6,9-dicarbadecaborane(14), dodecahydride-1-phenyl-1,3-dicarbanonaborane, dodecahydride-1-methyl-1,3-

dicarbanonaborane and undecahydride-1,3-dimethyl-1,3-dicarbanonaborane.

Furthermore, the following compounds can be also employed. (In the ionic compounds listed below, the counter ion is tri(n-butyl)ammonium, but not intended to limit thereto.)

Salts of metallic carboranes and metallic borane anions, for example, tri(n-butyl)ammoniumbis(nonahydride-1,3-dicarbanonaborate)cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)nickelate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)cuprate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)aurate(III), tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)chromate(III), tri(n-butyl)ammoniumbis(tribromooctahydride-7,8-dicarbaundecaborate)cobaltate(III), tri(n-butyl)ammoniumbis(dodecahydridedicarbadodecaborate)-cobaltate(III), bis[tri(n-butyl)ammonium]bis(dodecahydridedodecaborate)-

nickelate(III), tris[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)chromate(III), bis[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)manganate(IV), bis[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)cobaltate(III) and bis[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)nickelate(IV).

The compounds (B-3) which react with the transition metal compound (A) to form an ion pair can be used singly or in combination of two or more kinds.

In the present invention, at least one of the transition metal compound (A) and the activating compound (B) may be supported on a fine particle carrier.

The fine particle carrier is an inorganic or organic compound, and is a particulate or granular solid having a particle diameter of 10 to 300 μm, preferably 20 to 200 μm.

The inorganic carrier is preferably a porous oxide, and examples thereof include SiO_2, Al_2O_3, MgO, ZrO_2, TiO_2, B_2O_3, CaO, ZnO, BaO, ThO_2 and mixtures thereof, such as SiO_2-MgO, SiO_2-Al_2O_3, SiO_2-TiO_2, SiO_2-V_2O_5, SiO_2-Cr_2O_3 and SiO_2-TiO_2-MgO. Of these, preferred is a carrier containing at least one of SiO_2 and Al_2O_3 as its major component.

The above-mentioned inorganic oxides may contain carbonates, sulfates, nitrates and oxides, e.g., Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, Na_2SO_4, $Al_2(SO_4)_3$, $BaSO_4$, KNO_3, $Mg(NO_3)_2$, $Al(NO_3)_3$, Na_2O, K_2O and Li_2O, in small amounts.

The properties of the fine particle carrier vary depending on the type and the process for the preparation thereof, but preferably used in the invention is a carrier having a specific surface area of 50 to 1,000 m^2/g, preferably 100 to 700 m^2/g, and a pore volume of 0.3 to 2.5 cm^3/g. The fine particle carrier may be used after calcined at a temperature of 100 to 1,000 °C, preferably 150 to 700 °C, if desired.

Also employable as the fine particle carrier in the invention is a granular or particulate solid of an organic compound having a particle diameter of 10 to 300 μm. Examples of such organic compounds include (co)polymers produced mainly from α-olefins of 2 to 14 carbon atoms such as ethylene, propylene, 1-butene and 4-methyl-1-pentene, and (co)polymers produced mainly from vinylcyclohexane or styrene.

The fine particle carrier may contain a surface hydroxyl group and/or water.

The olefin polymerization catalyst used in the invention may be either a catalyst comprising the transition metal compound (A) supported on the fine particle carrier and the activating compound (B), a solid catalyst comprising the transition metal compound (A) and the activating compound (B) both supported on the fine particle carrier or a prepolymerized catalyst obtained by prepolymerizing an olefin in the presence of the transition metal compound (A), the activating compound (B) and the fine particle carrier.

The solid catalyst can be prepared by mixing and contacting the transition metal compound (A), the activating compound (B) and the fine particle carrier with each other in an inert hydrocarbon medium or an olefin medium.

Examples of the inert hydrocarbon media used for preparing the olefin polymerization catalyst include:

aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosine;

alicyclic hydrocarbons, such as cyclopentane, cyclohexane and methylcyclopentane;

aromatic hydrocarbons, such as benzene, toluene and xylene;

halogenated hydrocarbons, such as ethylene chloride, chlorobenzene and dichloromethane; and

mixtures of these hydrocarbons.

The order of mixing and contacting the above components may be optionally determined, but preferably,

the fine particle carrier is first mixed and contacted with the activating compound (B) and then with the transition metal compound (A);

a mixture of the activating compound (B) and the transition metal compound (A) is mixed and contacted with the fine particle carrier; or

the fine particle carrier, the activating compound (B) and water are mixed and contacted with each other and then with the transition metal compound (A).

For supporting the transition metal compound (A) on the fine particle carrier, there can be generally employed a method where the transition metal compound (A) and the fine particle carrier are mixed and contacted in a hydrocarbon medium.

More specifically, the following procedure may be carried out:

(1) The activating compound (B) is added to and mixed with a suspension of the fine particle carrier in a hydrocarbon medium, the mixture is filtered to remove the medium, and the resulting solid component is further mixed and contacted with the transition metal compound (A) in the form of a suspension or a solution in a hydrocarbon medium;

(2) The activating compound (B) is added to and mixed with a suspension of the fine particle carrier in an aromatic hydrocarbon medium followed by further adding an aliphatic hydrocarbon medium, and then the aromatic hydrocarbon medium is removed under a reduced pressure to precipitate an organoaluminum oxy-compound on the fine particle carrier. After removing the aliphatic hydrocarbon medium, the resulting solid component is further mixed and contacted with the transition metal compound (A) in the form of a suspension or a solution in a hydrocarbon medium; or

(3) The activating compound (B) and the transition metal compoud (A) are added to and mixed with a suspension of the fne particle carrier in a hydrocarbon medium, and then the medium is removed by filtration or evaporation.

In the mixing of the above components, the transition metal compound (A) is used in an amount of usually 10^{-6} to 5×10^{-3} mol, preferably 3×10^{-6} to 10^{-3} mol, based on 1 g of the fine particle carrier; and a concentration of the transition metal compound (A) is in the range of about 5×10^{-6} to 2×10^{-2} mol/liter, preferably 10^{-5} to 10^{-2} mol/liter. If the component (B-1) is used as the activating compound (B), an atomic ratio of aluminum in the component (B-1) to the transition metal in the transition metal compound (A), (Al/transition metal), is in the range of usually 10 to 3,000, preferably 20 to 2,000. If the component (B-2) is used, an atomic ratio of aluminum in the component (B-2) to the transition metal in the transition metal compound (A), (Al/transition metal), is in the range of usually 10 to 3,000, preferably 20 to 2,000. If the component (B-3) is used, a molar ratio of the transition metal compound (A) to the component (B-3), (transition metal compound (A)/component (B-3)), is in the range of usually 0.01 to 10, preferably 0.1 to 5.

In the mixing of the above components, the temperature is in the range of usually -50 to 150 °C, preferably -20 to 120 °C; and the contact time is in the range of 1 to 1,000 minutes, preferably 5 to 600 minutes. The mixing temperature may be varied during the mixing procedure.

Supporting of the transition metal compound (A) on the fine particle carrier can be carried out in the presence of zeolite or organic amines.

Zeolite used herein is, for example, a compound represented by the general formula

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

wherein M is Na, K, Ca or Ba, n is a valence of M, x is 2 to 10, and y is 2 to 7, and Molecular Sieve™ is preferred.

Examples of the organic amines include monoalkylamines, such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine and t-butylamine; dialkylamines, such as dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine and di-t-butylamine; and trialkylamines, such as trimethylamine, triethylamine, tri-n-propylamine and tri-n-butylamine.

Zeolite may be used in an amount of usually 1×10^{-2} to 1×10^{2} g, preferably 1×10^{-1} to 10 g, based on 1 g of the fine particle carrier. The organic amine may be used in an amount of usually 1×10^{-7} to 2×10^{-2} mol, preferably 1×10^{-5} to 1×10^{-2} mol, based on 1 g of the fine particle carrier.

The use of zeolite or the organic amine enables to produce a solid catalyst in which a larger amount of the transition metal compound (A) is supported.

In the solid catalyst obtained in the manner as described above, it is desired that the transition metal atom is supported in an amount of 10^{-6} to 10^{-3} g·atom, preferably 2×10^{-6} to 3×10^{-4} g·atom, based on 1 g of the

fine particle carrier, and the aluminum atom derived from the component (B-1) [or the component (B-2)] is supported in an amount of about 10^{-3} to 10^{-1} g·atom, preferably 2×10^{-3} to 5×10^{-2} g·atom, based on 1 g of the fine particle carrier. The component (B-3) is desirably supported in an amount of 10^{-7} to 0.1 g·atom, preferably 2×10^{-7} to 3×10^{-2} g·atom, based on 1 g of the fine particle carrier, in terms of the boron atom derived from the component (B-3).

The prepolymerized catalyst can be prepared by prepolymerizing a small amount of an olefin in an inert hydrocarbon medium or an olefin medium in the presence of the transition metal compound (A), the activating compound (B) and the fine particle carrier. It is preferred to use the transition metal compound (A), the activating compound (B) and the fine particle carrier in the form of a solid catalyst together as described above.

For preparing the prepolymerized catalyst, the inert hydrocarbon solvents as mentioned above can be employed.

In the preparation of the prepolymerized catalyst, the transition metal compound (A) is used in an amount of usually 10^{-6} to 5×10^{-3} mol, preferably 3×10^{-6} to 10^{-3} mol, based on 1 g of the fine particle carrier; and a concentration of the transition metal atom (A) is in the range of about 5×10^{-6} to 2×10^{-2} mol/liter-medium, preferably 10^{-5} to 10^{-2} mol/liter-medium. If the component (B-1) is used as the activating compound (B), an atomic ratio of aluminum in the component (B-1) to the transition metal in the transition metal compound (A), (Al/transition

metal), is in the range of usually 10 to 3,000, preferably 20 to 2,000. If the component (B-2) is used, an atomic ratio of aluminum in the component (B-2) to the transition metal in the transition metal compound (A), (Al/transition metal), is in the range of usually 10 to 3,000, preferably 20 to 2,000. If the component (B-3) is used, a molar ratio of the transition metal compound (A) to the component (B-3), (transition metal compound (A)/component (B-3)), is in the range of usually 0.01 to 10, preferably 0.1 to 5.

The prepolymerization temperature is in the range of -20 to 80 °C, preferably 0 to 60 °C; and the prepolymerization time is in the range of 0.5 to 100 hours, preferably about 1 to 50 hours.

The olefin used for the prepolymerization may be any one selected from those used for the polymerization, but preferred is the same monomer as used for the polymerization or a mixture of the same monomer as used for the polymerization and an olefin.

In the prepolymerized catalyst obtained as described above, it is desired that the transition metal atom is supported in an amount of 10^{-6} to 10^{-3} g·atom, preferably 2×10^{-6} to 3×10^{-4} g·atom, based on 1 g of the fine particle carrier, and the aluminum atom derived from the component (B-1) or the component (B-2) is supported in an amount of about 10^{-3} to 10^{-1} g·atom, preferably 2×10^{-3} to 5×10^{-2} g·atom, based on 1 g of the fine particle carrier. The component (B-3) is desirably supported in an amount of 10^{-7} to 0.1 g·atom, preferably 2×10^{-7} to 3×10^{-2} g·atom, based

on 1 g of the fine particle carrier, in terms of the boron atom derived from the component (B-3). The amount of a polymer produced by the prepolymerization is desired to be in the range of about 0.1 to 500 g, preferably 0.3 to 300 g, particularly preferably 1 to 100 g, based on 1 g of the fine particle carrier.

According to the present invention, multistage polymerization including the steps (a) and (b), which will be described later more in detail, is carried out in the presence of the olefin polymerization catalyst comprising the transition metal compound (A) and the activating compound (B), to prepare a propylene polymer composition. The polymerization steps may be carried out in any order, and the second stage polymerization is conducted in the presence of a polymer prepared in the first stage polymerization.

In the step (a), (i) propylene is homopolymerized, or (ii) propylene is copolymerized with at least one olefin selected from ethylene and olefins of 4 to 20 carbon atoms, in the presence of the olefin polymerization catalyst comprising the transition metal compound (A) and the activating compound (B), to prepare a propylene (co)polymer (a).

Examples of the olefins of 4 to 20 carbon atoms used herein include 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

The olefin used for the copolymerization of propylene is preferably ethylene or 1-butene. When ethylene or 1-butene is used, the resulting (co)polymer (a) is lowered in the glass transition temperature and thus the polymer composition obtained is improved in the impact resistance.

In the step (a), the polymerization can be carried out in a liquid phase polymerization, e.g., a suspension polymerization, and a gas phase polymerization.

In the liquid phase polymerization, the inert hydrocarbons same as used for the preparation of the catalyst described before, or the olefin itself can be used as a medium.

For the polymerization in the step (a), the transition metal compound (A) is desired to be used in an amount of usually 10^{-8} to 10^{-3} g·atom/liter, preferably 10^{-7} to 10^{-4} g·atom/liter, in terms of a concentration of the transition metal atom derived from the transition metal compound (A) in the polymerization system. If the component (B-1) is used as the activating compound (B), an atomic ratio of aluminum in the component (B-1) to the transition metal in the transition metal compound (A), (Al/transition metal), is in the range of usually 5 to 10,000, preferably 10 to 5,000. If the component (B-2) is used, an atomic ratio of aluminum in the component (B-2) to the transition metal in the transition metal compound (A), (Al/transition metal), is in the range of usually 5 to 10,000, preferably 10 to 5,000. If the component (B-3) is used, a molar ratio of the transition metal compound (A) to the component (B-3),

(transition metal compound (A)/component (B-3)), is in the range of usually 0.01 to 10, preferably 0.5 to 5.

When the solid catalyst or the prepolymerized catalyst is used, a compound selected from the component (B-1), the component (B-2) and the component (B-3), all of which are not supported on a fine particle carrier, may be used in addition to the activating compound (B) supported on a fine particle carrier.

The polymerization temperature is desired to be in the range of usually -50 to 100 °C, preferably 0 to 90 °C, in the case of slurry polymerization; in the range of usually 0 to 250 °C, preferably 20 to 200 °C, in the case of liquid phase polymerization; and in the range of usually 0 to 120 °C, preferably 20 to 100 °C, in the case of gas phase polymerization. The polymerization pressure is in the range of usually atmospheric pressure to 100 kg/cm^2, preferably atmospheric pressure to 50 kg/cm^2.

The molecular weight of the resulting propylene (co)polymer (a) can be regulated by the use of hydrogen in the polymerization system or varying the polymerization temperature.

The step (a) is carried out usually in a single stage, but the polymerization operation may be divided into plural stages to obtain a polymer containing two or more components greatly different from each other in the molecular weight. For example, the step (a) can be carried out in such a manner that a ratio of a melt flow rate of a polymer obtained in an initial stage of the step (a) to a

melt flow rate of a polymer obtained in a subsequent stage of the step (a) is not less than 20, in an extreme case, not less than 30.

The propylene (co)polymer (a) prepared in this step (a) comprises constituent units derived from propylene in amounts of not less than 80 mol%, preferably not less than 90 mol%, more preferably not less than 95 mol%, and is particularly preferably a propylene homopolymer. This propylene (co)polymer (a) has a melting point, as measured by a differential scanning calorimeter, of not lower than 100 °C, preferably not lower than 110 °C, more preferably not lower than 120°C, particularly preferably 130 to 167 °C. If the melting point is lower than 100 °C, the propylene (co)polymer may have a reduced heat resistance and lose characteristics required for propylene polymers. The propylene (co)polymer (a) has a melt flow rate, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 1,000 g/10 min, preferably 0.1 to 500 g/10 min. If the melt flow rate is less than 0.01 g/10 min, moldability of the polymer composition obtained may be reduced. If the melt flow rate exceeds 1,000 g/10 min, mechanical strength of the polymer composition obtained may also be reduced. The propylene (co)polymer (a) is desired to have a flexural modulus (FM) of not less than 5,000 kg/cm^2.

The melting point is measured using DSC-50 available from Shimazu Seisakusho in which a sample has been temporarily melted and cooled is heated at a heat-up rate of 10°C/min. The melt flow rate is measured in accordance

with ASTM D1238-T65 under the conditions of a temperature of 230 °C and a load of 2.16 kg.

In the step (b), ethylene is copolymerized with at least one olefin selected from olefins of 4 to 20 carbon atoms in the presence of an olefin polymerization catalyst comprising the transition metal compound (A) and the activating compound (B), to prepare an ethylene copolymer (b).

As the olefin of 4 to 20 carbon atoms, the aforesaid olefins of 4 to 20 carbon atoms can be employed.

The olefin used for the copolymerization of ethylene is preferably 1-butene. When 1-butene is used, the resulting ethylene copolymer (b) is lowered in the glass transition temperature and thus the polymer composition obtained is improved in the impact resistance.

In the step (b), the polymerization can be carried out in a liquid phase polymerization, e.g., a suspension polymerization, and a gas phase polymerization.

In the liquid phase polymerization, the inert hydrocarbon same as for the preparation of the catalyst described before, or the olefin itself can be used as a medium.

For the polymerization in the step (b), the transition metal compound (A) is desired to be used in an amount of usually 10^{-8} to 10^{-3} g·atom/liter, preferably 10^{-7} to 10^{-4} g·atom/liter, in terms of a concentration of the transition metal atom derived from the transition metal compound (A) in the polymerization system. If the component (B-1) is

used as the activating compound (B), an atomic ratio of aluminum in the component (B-1) to the transition metal in the transition metal compound (A), (Al/transition metal), is in the range of usually 5 to 10,000, preferably 10 to 5,000. If the component (B-2) is used, an atomic ratio of aluminum in the component (B-2) to the transition metal in the transition metal compound (A), (Al/transition metal), is in the range of usually 5 to 10,000, preferably 10 to 5,000. If the component (B-3) is used, a molar ratio of the transition metal compound (A) to the component (B-3), (transition metal compound (A)/component (B-3)), is in the range of usually 0.01 to 10, preferably 0.5 to 5.

When the solid catalyst or the prepolymerized catalyst is used, a compound selected from the component (B-1), the component (B-2) and the component (B-3), all of which are not supported on a fine particle carrier, may be used in addition to the activating compound (B) supported on a fine particle carrier.

The polymerization temperature is desired to be in the range of usually -50 to 100 °C, preferably 0 to 90 °C, in the case of slurry polymerization; in the range of usually 0 to 250 °C, preferably 20 to 200 °C, in the case of liquid phase polymerization; and in the range of usually 0 to 120 °C, preferably 20 to 100 °C, in the case of gas phase polymerization. The polymerization pressure is in the range of usually atmospheric pressure to 100 kg/cm^2, preferably atmospheric pressure to 50 kg/cm^2.

The molecular weight of the resulting ethylene copolymer can be regulated by the use of hydrogen in the polymerization system or varying the polymerization temperature.

The ethylene copolymer (b) prepared in the step (b) comprises constituent units derived from ethylene in amounts exceeding 50 mol%, preferably 55 to 90 mol%, more preferably 70 to 85 mol%. If the ethylene content is not more than 50 mol%, impact resistance of the polymer composition obtained may be lowered.

The ethylene copolymer (b) has an intrinsic viscosity [η], as measured in decalin at 135 °C, of 0.1 to 20 dl/g, preferably 1 to 10 dl/g, more preferably 2 to 5 dl/g. If the intrinsic viscosity [η] is less than 0.1 dl/g, impact resistance of the polymer composition obtained may also be lowered. If the intrinsic viscosity [η] exceeds 20 dl/g, moldability of the polymer composition obtained may be reduced. The ethylene copolymer (b) is desired to have a glass transition temperature of higher than -80 °C and up to -10 °C.

Further, it is desired that the ethylene copolymer (b) has a density of 0.85 to 0.91 g/cm^3, preferably 0.86 to 0.90 g/cm^3, an Mn/Mw value indicating a molecular weight distribution of 1.4 to 3.5, preferably 2.0 to 3.0, and a melt flow rate of 1.0 to 45 g/10 min, preferably 0.5 to 10 g/10 min.

According to the present invention, multistage polymerization including the steps (a) and (b) may be

carried out in any order, and the second stage polymerization is carried out in the presence of a polymer obtained in the first stage polymerization to prepare a propylene polymer composition.

In more detail, the multistage polymerization can be carried out as follows.

(1) The step (a) is first carried out in the presence of the transition metal compound (A) and the activating compound (B) to prepare a propylene (co)polymer (a), and then the step (b) is carried out in the presence of the transition metal compound (A), the activating compound (B) and the propylene (co)polymer (a) to prepare an ethylene copolymer (b), whereby a propylene polymer composition is prepared.

(2) The step (b) is first carried out in the presence of the transition metal compound (A) and the activating compound (B) to prepare an ethylene copolymer (b), and then the step (a) is carried out in the presence of the transition metal compound (A), the activating compound (B) and the ethylene copolymer (b) to prepare a propylene (co)polymer (a), whereby a propylene polymer composition is prepared.

In the present invention, it is preferred that the step (a) is first carried out and then the step (b). By the use of this order, aggromation of the resulting polymer particles or adhesion thereof to the reactor wall can be avoided due to their improved particle properties, so that

the propylene polymer composition can be obtained under stable operating conditions.

Each of the steps is carried out in such a manner that the resulting propylene polymer composition contains the propylene (co)polymer (a) obtained in the step (a) in an amount of 20 to 90 % by weight, preferably 30 to 80 % by weight, and the ethylene copolymer (b) obtained in the step (b) in an amount of 10 to 80 % by weight, preferably 20 to 70 % by weight. The propylene polymer composition obtained has a melt flow rate, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 500 g/10 min, preferably 0.1 to 200 g/10 min. If the melt flow rate is less than 0.01 g/10 min, moldability of the polymer composition may be reduced. If the melt flow rate exceeds 500 g/10 min, mechanical strength of the polymer composition may be lowered.

Particularly preferred embodiments of the process for preparing a propylene polymer composition according to the invention are as follows.

(1) A process for preparing a propylene polymer composition, wherein the step (a) is carried out in the presence of an olefin polymerization catalyst comprising the transition metal compound (A) represented by the formula (II), the organoaluminum oxy-compound (B-2), and optionally, the organoaluminum compound (B-1), to prepare a propylene homopolymer, and then the step (b) is carried out in the presence of the above-mentioned olefin polymerization catalyst and the propylene homopolymer, to prepare an ethylene-1-butene copolymer containing

constituent units derived from ethylene in amounts of 55 to 90 % by mol.

(2) A process for preparing a propylene polymer composition, wherein the step (a) is carried out in the presence of an olefin polymerizaton catalyst comprising the transition metal compound (A) represented by the formula (III), the organoaluminum oxy-compound (B-2), and optionally, the organoaluminum compound (B-1), to prepare a propylene homopolymer, and then the step (b) is carried out in the presence of the above-mentioned olefin polymerization catalyst and the propylene homopolymer, to prepare an ethylene-1-butene copolymer containing constituent units derived from ethylene in amounts of 55 to 90 % by mol.

The propylene polymer composition obtained by the process of the invention has well balanced properties among rigidity, heat resistance and impact resistance. Such propylene polymer composition is favorably used for various molded artifcles including films and sheets in many fields.

EFFECT OF THE INVENTION

The process for preparing a propylene polymer composition according to the invention can prepare a propylene polymer composition which has well balanced properties among rigidity, heat resistance and impact resistance.

The propylene polyemer composition according to the invention has well balanced properties among rigidity, heat resistance and impact resistance.

EXAMPLE

The present invention will be further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

In the following examples, properties of the propylene polymer composition were measured by the methods described below.

Flexural modulus (FM)

Measured in accordance with ASTM D790.

Specimen: 12.7 mm (width) × 6.4 mm (thickness) × 127 mm (length).

Span: 100 mm.

Flexural speed: 2 mm/min.

Izod impact strength (IZ)

Measured in accordance with ASTM D256.

Temperature: -30 °C, 23 °C.

Specimen: 12.7 mm (width) × 6.4 mm (thickness) × 64 mm (length), mechanically notched.

Tensile elongation at break (EL)

Measured in accordance with ASTM D638.

Temperature: 23 °C.

Heat distortion temperature (HDT)

Measured in accordance with ASTM D648.

Specimen: 12.7 mm (width) × 6.4 mm (thickness) × 127 mm (length).

Haze

Measured in accordance with ASTM D1003-61.

Preparation Example 1

Synthesis of rac-dimethylsilyl-bis{1-(2-n-propyl-4-(9-phenanthryl)indenyl)zirconium dichloride

[Synthesis of 3-(2-bromophenyl)-2-n-propylpropionic acid]

A 1-liter four-necked round flask (equipped with stirrer, Dimroth condenser, dropping funnel and thermometer) was charged with 37 g (330 mmol) of potassium t-butoxide, 32 ml (334 mmol) of N-methylpyrrolidone and 400 ml of toluene. Then, the flask was placed in an ice bath, and a solution obtained by dissolving 60.7 g (300 mmol) of diethyl n-propylmalonate in 50 ml of toluene dropwise added while stirring (dropping time: 30 minutes, reaction temperature: 5 to 10 °C). After the dropping was completed, the mixture was stirred at 45 °C for 30 minutes and then at 65 °C for 1 hour. Immediately after starting

of the heating, the reaction solution turned cream-colored and heterogeneous.

Subsequently, in an ice bath, a solution obtained by dissolving 75 g (300 mmol) of 2-bromobenzyl bromide in 50 ml of toluene was dropwise added (dropping time: 30 minutes, reaction temperature: 5 to 15 °C). After the dropping was completed, the mixture was reacted at 65 °C for 30 minutes, and then heated under reflux for 1 hour. The color of the reaction mixture was gradually changed to gray. After the reaction mixture was allowed to stand for cooling, it was poured into 500 ml of water, and a 10 % aqueous solution of sulfuric acid was added to adjust pH = 1. The organic phases were separated, and the aqueous phase was extracted five times with 100 ml of toluene. The combined organic phases were washed four times with 200 ml of a saturated saline solution and dried over anhydrous $MgSO_4$, and the solvent was distilled off to obtain 114 g of a brown liquid concentrate.

A 2-liter four-necked round flask (equipped with stirrer, Dimroth condenser, dropping funnel and thermometer) was charged with the concentrate obtained above and 200 ml of methanol, and they were stirred. To the flask was added a solution obtained by dissolving 237 g of potassium hydroxide (content of potassium hydroxide: 85 %, 3.59 mol) in 520 ml of methanol and 180 ml of water. Then, the flask was placed in an oil bath at 90 °C, the mixture was refluxed for 5 hours, most of methanol was distilled off by an evaporator, and 500 ml of water was

added to give a homogeneous solution to which, under ice cooling, a 10 % aqueous solution of sulfuric acid was added to adjust pH = 1, and a white solid precipitated was separated by filtration. Then, the organic phase was separated from the filtrate, and the aqueous phase was extracted six times with 200 ml of ether. The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was distilled off to obtain 94 g of an yellow white semisolid.

Subsequently, the semisolid was introduced to a 1-liter round flask, heated at 180°C (oil bath temperature) for 10 minutes, and then cooled to obtain 78.0 g of the aimed product as a brown transparent liquid (yield: 96 %). The properties of the product thus obtained are described below.

FD-MS: 270 (M^+), 272 (M^+ +2)

NMR ($CDCl_3$, 90 MHz):

δ = 0.95 (t, J = 7.0 Hz, 3H, CH_3);

1.10 - 2.00 (m, 4H);

2.60 - 3.25 (m, 3H);

6.90 - 7.80 (m, 4H)

[Synthesis of 3-(bromophenyl)-2-n-propylpropionyl chloride]

A 500-ml three-necked round flask (equipped with stirrer tip, Dimroth condenser, thermometer and NaOH trap) was charged with 277 mmol of 3-(2-bromophenyl)-2-n-propylpropionic acid and 200 ml of thionyl chloride, and they were heated under reflux for 2 hours. After the

thionyl chloride was distilled off by single distillation, a vacuum distillation gave 77.4 g of a crude product as a light brown transparent liquid having a boiling point of 130 to 135 °C/1 mmHg. This acid chloride was used for the next reaction without further purification.

[Synthesis of 4-bromo-2-n-propyl-1-indanone]

A 1-liter four-necked round flask (equipped with stirrer tip, Dimroth condenser, dropping funnel, thermometer and NaOH trap) was charged with 74.5 g (559 mmol) of anhydrous aluminum chloride and 400 ml of carbon disulfide. Under ice cooling, a solution obtained by dissolving the above acid chloride in 100 ml of carbon disulfide was dropwise added slowly. After the dropping was completed, the mixture was further reacted for 3 hours under ice cooling. Then, the reaction solution was poured into 600 ml of ice water to separate the organic phase, and the aqueous phase was extracted four times with 200 ml of ether. The combined organic phases were washed four times with 300 ml of a saturated sodium hydrogencarbonate solution and dried over anhydrous $MgSO_4$, and the solvent was distilled off to obtain 66.7 g of a brown liquid. This ketone was used for the next reaction without further purification.

[Synthesis of 4-bromo-2-n-propyl-1-trimethylsilyloxyindan]

A 1-liter four-necked round flask (equipped with stirrer tip, Dimroth condenser, dropping funnel and

thermometer) was charged with 4.96 g (131 mmol) of sodium boron hydride and 300 ml of ethanol. Under ice cooling, a solution obtained by dissolving 4-bromo-2-n-propyl-1-indanone obtained above in 200 ml of ethanol was dropwise added. After the dropping was completed, the mixture was further reacted for 3 hours at room temperature. After the reaction, 200 ml of ice water was added, and most of methanol was distilled off by an evaporator. The residue was transferred into a separatory funnel with 300 ml of ether, the organic phase was separated, and the aqueous phase was extracted three times with 200 ml of ether. The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was distilled off to obtain 66.50 g of an yellow white powder.

Subsequently, a 1-liter four-necked round flask was charged with the yellow white powder obtained above, 200 ml of ether and 47 ml (337 mmol) of triethylamine. Under ice cooling, a solution obtained by dissolving 39 ml (307 mmol) of trimethylsilyl chloride in 50 ml of ether was dropwise added slowly. After the 7 hours reaction, the reaction mixture was poured into 400 ml of a saturated sodium hydrogencarbonate solution, the organic phase was separated, and the aqueous phase was extracted three times with 200 ml of ether. The combined organic phases were washed with 400 ml of a saturated saline solution and dried over anhydrous $MgSO_4$, the solvent was distilled off to obtain an yellow brown liquid. A vacuum distillation gave 76.00 g of the aimed product having a boiling point of 120

to 125 °C/2 mmHg as a light yellow white transparent liquid. The yield summed up from 3-(2-bromophenyl)-2-n-propylpropionic acid was 81 %.

[Synthesis of 2-n-propyl-4-(9-phenanthryl)indene]

A 300-ml four-necked round flask (equipped with stirrer tip, dropping funnel and thermometer) was charged with 10 g (30.5 mmol) of 4-bromo-2-n-propyl-1-trimethylsilyloxyindan obtained above, 50 ml of anhydrous ether and 112 mg (0.153 mmol) of $PdCl_2$ (dppf). To the flask was then dropwise added slowly 42 ml (61 mmol) of a 1.45 molar 9-phenanthrylmagnesium bromide in ether/benzene, while stirring at room temperature. Thereafter, the internal temperature was elevated to 42 °C, the reaction mixture was refluxed for 10 hours, poured into 300 ml of a saturated aqueous solution of ammonium chloride and extracted four times with 200 ml of ether. The combined organic phases were washed with a saturated saline solution and dried over anhydrous $MgSO_4$, and the solvent was distilled off to obtain 20.32 g of a brown liquid.

A 300-ml four-necked round flask was charged with the brown liquid obtained above and 50 ml of ether, and 60 ml of a 5N aqueous solution of hydrochloric acid was dropwise added at room temperature, followed by vigorous stirring. After 6.5 hours, the reaction solution was transferred into a separatory funnel, extracted four times with 50 ml of ether, the combined organic phases were washed twice with 100 ml of a saturated sodium hydrogencarbonate solution and

dried over anhydrous $MgSO_4$, and the solvent was distilled off to obtain a brown semisolid which was purified by silica gel chromatography to obtain 10.75 g of an yellow powder.

Subsequently, a 200-ml four-necked round flask was charged with the yellow powder obtained above, 80 ml of anhydrous methylene chloride, 12.8 ml (92.0 mmol) of triethylamine and 187 ml (1.53 mmol) of 4-dimethylaminopyridine. Under ice cooling, a solution obtained by dissolving 4.72 ml (61.0 mmol) of methanesulfonyl chloride in 20 ml of anhydrous methylene chloride was dropwise added slowly. After the dropping was completed, the temperature of the mixture was elevated to room temperature and then the reaction was carried out for 4 hours. The reaction mixture was poured into 100 ml of ice water, extracted three times with 100 ml of methylene chloride, the combined organic phases were washed three times with 100 ml of a saturated sodium hydrogencarbonate solution and dried over anhydrous $MgSO_4$. Then, the solvent was distilled off to obtain a red brown semisolid which was purified by silica gel chromatography to obtain 7.20 g of the aimed product as an yellow white powder (yield: 71 %). The properties of the product thus obtained are described below.

NMR ($CDCl_3$, 90 MHz):

δ = 0.92 (t, J = 7.0 Hz, 3H, CH_3);

1.50 (m, 2H);

2.36 (t, J = 7.0 Hz, 2H);

3.02 (bd, 2H);

6.60 (s, 1H);

7.05 - 9.00 (m, 12H)

[Synthesis of dimethylsilylene-bis{1-(2-n-propyl-4-(9-phenanthryl)indene)}]

A 300-ml four-necked round flask (equipped with stirrer tip, Dimroth condenser, dropping funnel and thermometer) was charged with 6.20 g (18.5 mmol) of the 2-n-propyl-4-(9-phenanthryl)indene obtained above, 120 ml of anhydrous ether and 50 mg of copper cyanide. Under ice cooling, 12.5 ml (20.4 mmol) of a 1.63 molar n-butyllithium in hexane was dropwise added. After the dropping was completed, the content in the flask was refluxed for 1.5 hours. Then, under ice cooling, a solution of 1.34 ml (11.1 mmol) of dimethyldichlorosilane in 10 ml of anhydrous ether was dropwise added slowly. After the dropping was completed, the reaction was carried out overnight at room temperature, and then the reaction mixture was poured into 200 ml of a saturated aqueous ammonium chloride. After filtration, the filtrate was extracted three times with 100 ml of ether, the organic phase was washed with 200 ml of a saturated saline solution and dried over anhydrous $MgSO_4$, and the solvent was distilled off to obtain an yellow white powder which was purified by silica gel chromatography to obtain 3.80 g of the aimed product as an yellow white powder (yield: 54 %). The properties of the product thus obtained are described below.

NMR ($CDCl_3$, 90 MHz):

δ = -0.17, -0.15 (each: s, together 6H, Si-CH_3);

0.65 - 2.75 (m, 14H);

3.86 - 4.25 (m, 2H, -CH-Si);

6.25, 6.34 (each: 6d, 2H);

7.05 - 9.05 (m, 24H)

[synthesis of rac-dimethylsilyl-bis{1-(2-n-propyl-4-(9-phenanthryl)indenyl)}zirconium dichloride]

A 200-ml four-necked round flask (equipped with stirrer tip, bead condenser, dropping funnel and thermometer) was charged with 2.9 g (4.00 mmol) of dimethylsilyl-bis{1-(2-n-propyl-4-(9-phenanthryl)indene)} and 60 ml of anhydrous ether. Under ice cooling, 5.15 ml (8.40 mmol) of a 1.63 molar n-butyllithium in hexane was dropwise added slowly. After the dropping was completed, the content in the flask was stirred overnight at room temperature, and 1.00 g (4.29 mmol) of $ZrCl_4$ was added in portions at -78 °C. After the addition was completed, the mixture was allowed to stand overnight to elevated the temperature. The resulting orange reaction slurry was filtered, the filter cake was washed with 100 ml of anhydrous methylene chloride, and the fltrate was concentrated to dryness. The resulting product was redissolved in 100 ml of anhydrous methylene chloride, and anhydrous ether was added to the solution. The solid precipitated was filtered, washed with 15 ml of anhydrous ether and dried under reduced pressure to obtain 0.10 g of

the aimed product as an yellow powder (yield: 2.8 %). The properties of the product thus obtained are described below.

NMR ($CDCl_3$, 90 MHz):

δ = 0.80 (t, J = 7.4 Hz, 6H, CH_3);

1.39 (s, 6H, Si-CH_3);

1.10 - 3.00 (m, 8H);

6.61 (s, 2H, 3-H-Ind);

7.00 - 9.10 (m, 24 H)

Example 1

[Preparation of solid aluminoxane component (a)]

A 300-ml pressure-reducible reactor equipped with a stirrer was charged with 67 ml of a toluene solution containing methylaluminoxane corresponding to 100 mmol of aluminum atom (methylaluminoxane available from Shelling Co.), and then added 100 ml of purified n-decane at room temperature over a period of about 0.5 hour with stirring, to precipitate methylaluminoxane. Then, toluene was removed from the reactor by elevating the temperature in the reactor to 35 °C over a period of about 3 hours under a reduced internal pressure of 4 Torr using a vacuum pump, to further precipitate aluminoxane. The reaction solution was filtered to remove the liquid phase, and the solid was resuspended in n-decane to obtain an aluminoxane suspension containing 0.18 mmol-Al/ml [solid aluminoxane component (a)].

[Preparation of solid catalyst component (b-1)]

A 400-ml reactor thoroughly purged with nitrogen was charged with 100 ml of n-hexane, and 10.5 mmol (in terms of Al atom) of the solid aluminoxane component (a) obtained above and 0.07 mmol (in terms of Zr atom) of rac-dimethylsilyl-bis{1-(2-n-propyl-4-(9-phenanthryl)indenyl)}zirconium dichloride, and then the mixture was stirred for 20 minutes. 100 ml of n-hexane and 0.9 mmol of triisobutylaluminum were added, followed by stirring for 10 minutes. Then, a propylene gas was passed through the reactor at 20°C for 4 hours at a rate of 2.2 l/hr to prepolymerize propylene. The supernatant was removed by decantation, and the remainder was washed three times with 150 ml of decane. As a result, a solid catalyst component (b-1) in which Zr and Al were supported in amounts of 0.010 mmol and 4.3 mmol, respectively, based on 1 g of the solid catalyst was obtained.

[Polymerization]

A 2-liter stainless steel autoclave was charged with 500 g of propylene and 4.5 liters of hydrogen at room temperature, and the temperature was elevated to 40 °C. Then, 0.5 mmol of triisobutylaluminum and 0.004 mmol (in terms of Zr atom) of the solid catalyst component (b-1) obtained above were added, to polymerize propylene at 50 °C for 25 minutes.

Subsequently, the internal pressure was released to atmospheric pressure, and nitrogen was passed through the

system for about 10 minutes to purge the system. During this procedure, 5.1 g of a polymer produced was taken out of the system by means of a specially devised sampler. Then, 150 ml of hydrogen and an ethylene/1-butene mixed gas (ethylene: 32 mol%, 1-butene: 68 mol%) were fed to the system so that the total pressure became 7 kg/cm^2. The polymerization was carried out at 50 °C for 20 minutes, while keeping the total pressure at 7 kg/cm^2 by continuous feeding the mixed gas. After the reaction was completed, the pressure was released to atmospheric pressure, giving 132 g of a white powdery polymer.

The propylene homopolymer obtained in the first stage had a melting point of 161 °C and MFR of 24 g/10 min, and the ethylene-1-butene copolymer obtained in the second stage had an ethylene content of 78 mol% and an intrinsic viscosity [η] of 2.5 dl/g.

The resulting propylene polymer composition contained the propylene homopolymer in an amount of 72 % by weight and the ethylene-1-butene copolymer in an amount of 28 % by weight, and had MFR of 16 g/10 min, IZ at 23 °C of 35 kg·cm/cm, FM of 11,300 kg/cm^2, EL of 350 % and HDT of 105 °C.

The amount, the composition, etc. of the polymer obtained in each stage were determined in the following manner. The melting point and MFR of the propylene homopolymer (P-1) obtained in the first stage were measured for a polymer (A-1) sampled after completion of the first stage polymerization. Further, a polymer (A-2) sampled

after completion of the second stage polymerization was immersed in 200 ml of boiling n-decane for 5 hours to dissolve the polymer and then cooled to room temperature to precipitate a solid which was filtered through a glass filter, then dried and measured on its weight. An NMR analysis on this dried solid proved that the ethylene content was lower than the lower limit of detection. Accordingly, a percent weight of the dried solid (i.e., the n-decane-insoluble portion at room temperature) to the weight of the polymer (A-2), can be taken as the % by weight of the propylene homopolymer (P-1). The n-decane-soluble portion in the polymer (A-1) was not more than 0.1 % by weight. On the other hand, the filtrate obtained by the above filtration of the polymer (A-2) was added to a large amount of methanol to precipitate a solid which was washed with methanol and dried to obtain a n-decane-soluble portion, which was taken as the ethylene-1-butene polymer (P-2) obtained in the second stage. This solid was measured on the intrinsic viscosity and the composition in accordance with a conventional NMR method.

Example 2

[Polymerization]

A 2-liter stainless steel autoclave was charged with 400 g of propylene, 0.6 liter of hydrogen and 16 liters of ethylene at room temperature, and the temperature was elevated to 50 °C. Then, 0.5 mmol of triisobutylaluminum and 0.004 mmol (in terms of zirconium atom) of the solid

catalyst component (b-1) prepared in Example 1 were added, and the polymerization was carried out at 60 °C for 25 minutes.

Subsequently, the internal pressure was released to atmospheric pressure, and nitrogen was passed through the system for about 10 minutes to purge the system. During this procedure, 5.1 g of a polymer produced was taken out of the system by means of a specially devised sampler. Then, 200 ml of hydrogen and an ethylene/1-butene mixed gas (ethylene: 38 % by mol, 1-butene: 62 % by mol) were fed to the system so that the total pressure became 5 kg/cm^2. The polymerization was carried out at 50 °C for 20 minutes, while keeping the total pressure at 5 kg/cm^2 by continuous feeding the mixed gas. After the reaction was completed, the pressure was released to atmospheric pressure, giving 136 g of a white powdery polymer.

The propylene homopolymer obtained in the first stage had a melting point of 128 °C and MFR of 6 g/10 min, and the ethylene-1-butene copolymer obtained in the second stage had an ethylene content of 85 mol% and an intrinsic viscosity [η] of 1.8 dl/g.

The resulting propylene polymer composition contained the propylene homopolymer in an amount of 69 % by weight and the ethylene-1-butene copolymer in an amount of 31 % by weight, and had MFR of 3.5 g/10 min, IZ at 23 °C of 58 kg·cm/cm, IZ at -30 °C of 11 kg·cm/cm, FM of 5,300 kg/cm^2, EL of 800 %, HDT of 85 °C and a haze, as measured for a square plate of 1 mm thick, of 41 %.

Example 3

[Polymerization]

A 2-liter stainless steel autoclave was chaged with 400 g of propylene, 0.6 liter of hydrogen and 16 liters of ethylene at room temperature, and the temperature was elevated to 50 °C. Then, 0.5 mmol of triisobutylaluminum and 0.004 mmol (in terms of zirconium atom) of the solid catalyst component (b-1) prepared in Example 1 were added, and the polymerization was carried out at 60 °C for 25 minutes.

Subsequently, the internal pressure was released to atmospheric pressure, and nitrogen was passed through the system for about 10 minutes to purge the system. During this procedure, 5.1 g of a polymer produced was taken out of the system by means of a specially devised sampler. Then, 90 ml of hydrogen and 200 ml of 1-octene were added, and ethylene was further fed so that the total pressure became 8 kg/cm^2. The polymerization was carried out at 60 °C for 30 minutes, while keeping the total pressure at 8 kg/cm^2 by continuous feeding ethylene. After the reaction was completed, the internal pressure was released to atmospheric pressure and the product was dried under reduced pressure, giving 130 g of a white powdery polymer.

The propylene homopolymer obtained in the first stage had a melting point of 128 °C and MFR of 6 g/10 min, and the ethylene-1-octene copolymer obtained in the second

stage had an ethylene content of 85 % by mol and an intrinsic viscosity [η] of 1.9 dl/g.

The resulting propylene polymer composition contained the propylene homopolymer in an amount of 72 % by weight and the ethylene-1-octene copolymer in an amount of 28 % by weight, and had MFR of 3.4 g/10 min, IZ at 23 °C of 60 kg·cm/cm, IZ at -30 °C of 12 kg·cm/cm, FM of 5,500 kg/cm², EL of 1,000 %, HDT of 85 °C and a haze, as measured for a square plate of 1 mm thick, of 40 %.

Comparative Example 1

[Polymerization]

A 2-liter stainless steel autoclave was charged with 400 g of propylene, 0.6 liter of hydrogen and 16 liters of ethylene at room temperature, and the temperature was elevated to 50 °C. Then, 0.5 mmol of triisobutylaluminum and 0.004 mmol (in terms of zirconium atom) of the solid catalyst component (b-1) prepared in Example 1 were added, and the polymerization was carried out at 60 °C for 25 minutes.

Subsequently, the internal pressure was released to atmospheric pressure, and nitrogen was passed through the system for about 10 minutes to purge the system. During this procedure, 5.1 g of a polymer produced was taken out of the system by means of a specially devised sampler. Then, 150 ml of hydrogen and an ethylene/propylene mixed gas (ethylene: 30 mol%, propylene: 70 mol%) were fed to the system so that the total pressure became 8 kg/cm². The

polymerization was carried out at 50 °C for 30 minutes, while keeping the total pressure at 8 kg/cm^2 by continuous feeding the mixed gas. After the reaction was completed, the pressure was released to atmospheric pressure, giving 168 g of a white powdery polymer.

The propylene homopolymer obtained in the first stage had a melting point of 128 °C and MFR of 6 g/10 min, and the ethylene-propylene copolymer obtained in the second stage had an ethylene content of 86 % by mol and an intrinsic viscosity [η] of 1.8 dl/g.

The resulting polymer composition contained the propylene homopolymer in an amount of 67 % by weight and the ethylene-propylene copolymer in an amount of 33 % by weight, and had MFR of 3.4 g/10 min, IZ at 23 °C of 50 kg·cm/cm, IZ at -30 °C of 6 kg·cm/cm, FM of 5,500 kg/cm^2, EL of 600 %, HDT of 85 °C and a haze, as measured for a square plate of 1 mm thick, of 80 %.

Example 4

[Preparation of solid catalyst component (b-2)]

A 400-ml reactor thoroughly purged with nitrogen was charged with 100 ml of n-hexane, and 10.5 mmol (in terms of Al atom) of the solid aluminoxane component (a) obtained in Example 1 and 0.07 mmol (in terms of Zr atom) of rac-dimethylsilyl-bis{1-(2-methyl-4-(phenyl)indenyl)}zirconium dichloride was added and then the mixture was stirred for 20 minutes. 100 ml of n-hexane and 0.9 mmol of triisobutylaluminum were added, followed by stirring for 10

minutes. Then, a propylene gas was passed through the reactor at 20°C for 4 hours at a rate of 2.2 l/hr to prepolymerize propylene. The supernatant was removed by decantation, and the remainder was washed three times with 150 ml of decane. As a result, a solid catalyst component (b-2) in which Zr and Al were supported in amounts of 0.010 mmol and 4.3 mmol, respectively, based on 1 g of the solid catalyst was obtained.

[Polymerization]

A 2-liter stainless steel autoclave was charged with 500 g of propylene and 0.8 liters of hydrogen at room temperature, and the temperature was elevated to 40 °C. Then, 0.5 mmol of triisobutylaluminum and 0.002 mmol (in terms of Zr atom) of the solid catalyst component (b-2) obtained above were added, to polymerize propylene at 50 °C for 25 minutes.

Subsequently, the internal pressure was released to atmospheric pressure, and nitrogen was passed through the system for about 10 minutes to purge the system. During this procedure, 5.1 g of a polymer produced was taken out of the system by means of a specially devised sampler. Then, 60 ml of 1-butene was added, and ethylene was fed to the system so that the total pressure became 8 kg/cm^2. The polymerization was carried out at 80 °C for 20 minutes, while keeping the total pressure at 8 kg/cm^2 by continuous feeding ethylene. After the reaction was completed, the

pressure was released to atmospheric pressure, giving 145 g of a white powdery polymer.

The propylene homopolymer obtained in the first stage had a melting point of 156 °C and MFR of 6.0 g/10 min, and the ethylene-1-butene copolymer obtained in the second stage had an ethylene content of 85 mol% and an intrinsic viscosity [η] of 3.0 dl/g.

The resulting propylene polymer composition contained the propylene homopolymer in an amount of 71 % by weight and the ethylene-1-butene copolymer in an amount of 29 % by weight, and had MFR of 1.8 g/10 min, IZ at 23 °C of 35 kg·cm/cm, FM of 10,200 kg/cm^2, EL of 400 % and HDT of 98 °C.

Example 5

[Polymerization]

A 2-liter stainless steel autoclave was charged with 500 g of propylene and 0.8 liter of hydrogen at room temperature, and the temperature was elevated to 40 °C. Then, 0.5 mmol of triisobutylaluminum and 0.002 mmol (in terms of zirconium atom) of the above solid catalyst component (b-2) were added, and the polymerization was carried out at 50 °C for 25 minutes.

Subsequently, the internal pressure was released to atmospheric pressure, and nitrogen was passed through the system for about 10 minutes to purge the system. During this procedure, 4.8 g of a polymer produced was taken out of the system by means of a specially devised sampler.

Then, 140 ml of 1-octene was added, and ethylene was fed to the system so that the total pressure became 8 kg/cm^2. The polymerization was carried out at 80 °C for 30 minutes, while keeping the total pressure at 8 kg/cm^2 by continuous feeding ethylene. After the reaction was completed, the pressure was released to atmospheric pressure, giving 133 g of a white powdery polymer.

The propylene homopolymer obtained in the first stage had a melting point of 156 °C and MFR of 6.0 g/10 min, and the ethylene-1-octene copolymer obtained in the second stage had an ethylene content of 82 mol% and an intrinsic viscosity [η] of 2.4 dl/g.

The resulting propylene polymer composition contained the propylene homopolymer in an amount of 78 % by weight and the ethylene-1-octene copolymer in an amount of 12 % by weight, and had MFR of 45 g/10 min, IZ at 23 °C of 13 kg·cm/cm, FM of 13,900 kg/cm^2, EL of 180 %, HDT of 118 °C.

What is claimed is:

1. A process for preparing a propylene polymer composition, comprising:

conducting multistage polymerization including the following steps (a) and (b) in the presence of

(A) a transition metal compound containing a ligand having a cyclopentadienyl skeleton and

(B) a compound activating the transition metal compound (A),

in which the steps (a) and (b) may be carried out in any order, and the second stage polymerization is carried out in the presence of a polymer obtained by the first stage polymerization to produce a propylene polymer composition comprising 20 to 90 % by weight of a propylene (co)polymer (a) obtained in the step (a) and 10 to 80 % by weight of an ethylene copolymer (b) obtained in the step (b), said composition having a melt flow rate, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 500 g/10 min;

the step (a):

(i) homopolymerizing propylene or (ii) copolymerizing propylene and at least one olefin selected from ethylene and olefins of 4 to 20 carbon atoms to prepare a propylene (co)polymer (a) comprising not less than 80 mol % of constituent units derived from propylene, said propylene (co)polymer (a) having a melting point, as measured by a differential scanning calorimeter, of not lower than 100 °C

and a melt flow rate, as measured at 230 °C under a load of 2.16 kg, of 0.01 to 1,000 g/10 min;

the step (b):

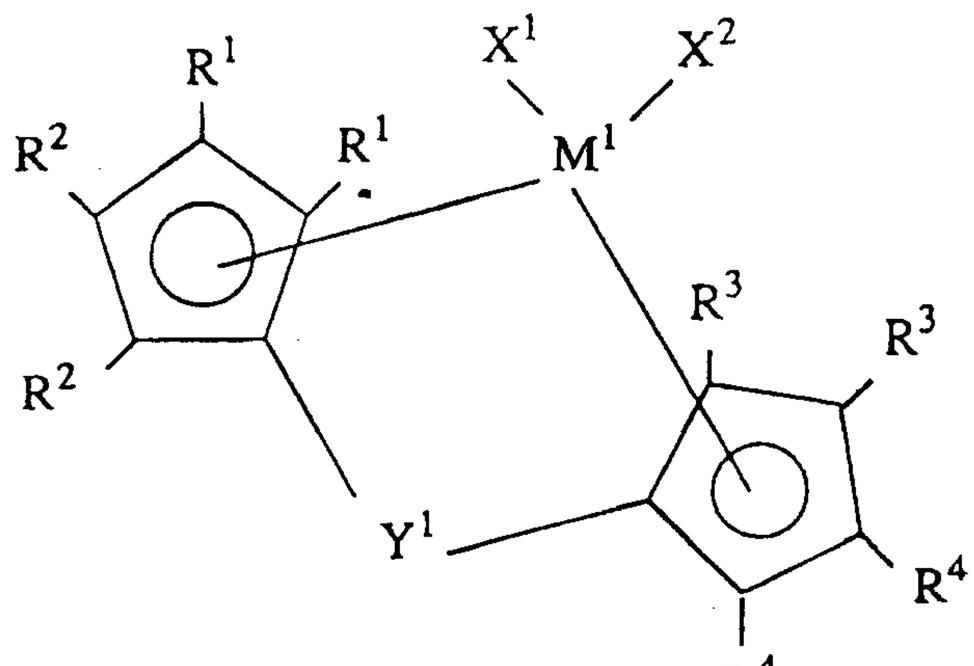
copolymerizing ethylene and at least one olefin selected from olefins of 4 to 20 carbon atoms to prepare an ethylene copolymer (b) comprising more than 50 mol % of constituent units derived from ethylene, the ethylene copolymer (b) having an intrinsic viscosity [η], as measured in decalin at 135 °C, of 0.1 to 20 dl/g.

2. The process for preparing a propylene polymer composition as claimed in Claim 1, wherein the ethylene copolymer (b) prepared in the step (b) has an intrinsic viscosity [η], as measured in decalin at 135°C, of 0.1 to 20 dl/g, a density of 0.85 to 0.91 g/cm^3, an Mn/Mw value indicating a molecular weight distribution of 1.4 to 3.5, and a melt flow rate of 0.1 to 45 g/10 min.

3. The process for preparing a propylene polymer composition as claimed in Claim 1 or 2, wherein the multistage polymerization is carried out in the order of the step (a) and the step (b).

4 The process for preparing a propylene polymer composition as claimed in any one of Claims 1 to 3, wherein propylene is homopolymerized in the step (a) and ethylene is copolymerized with 1-butene in the step (b).

5. The process for preparing a propylene polymer composition as claimed in any one of claims 1 to 4, wherein the transition metal compound (A) containing a ligand having a cyclopentadienyl skeleton is a compound represented by the following formula (II):



(II)

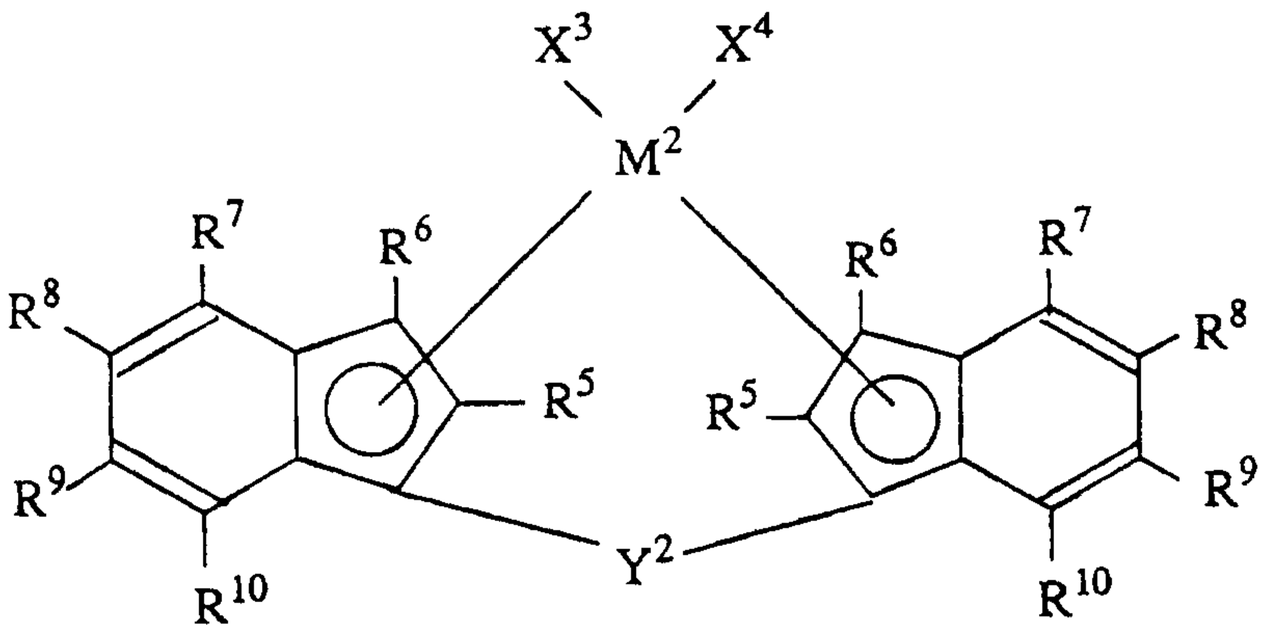
wherein M^1 is a transition metal atom of Group IVB to Group VIB of the periodic table;

R^1, R^2, R^3 and R^4 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group, wherein two adjacent groups among R^1, R^2, R^3 and R^4 may be bonded to form together with the carbon atoms to which they are attached a ring, and two adjacent groups represented by identical symbols, may be the same or different;

Y^1 is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group; and

X^1 and X^2 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group or a sulfur-containing group.

6. The process for preparing a propylene polymer composition as claimed in any one of claims 1 to 4, wherein the transition metal compound (A) containing a ligand having a cyclopentadienyl skeleton is a compound represented by the following formula (III):



(III)

wherein M^2 is a transition metal atom of group IVB to Group VIB of the periodic table;

R^5, R^6 and R^8 to R^{10}, which may be the same or different, are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, a silicon-containing group,

an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group;

R^7 is an aryl group of 6 to 16 carbon atoms;

Y^2 is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group; and

X^3 and X^4 are each a hydrogen, a halogen, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group or a sulfur-containing group.

7. The process for preparing a propylene polymer composition as claimed in any one of Claims 1 to 6, wherein the compound (B) activating the transition metal compound (A) is at least one compound selected from the group consisting of:

(B-1) an organoaluminum compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair.

8. A propylene polymer composition prepared according to the process as claimed in Claim 1.

9. The process as claimed in any one of claims 1 to 3, wherein:

the transition metal compound (A) is represented by the formula:

$$ML_x \qquad (I)$$

(wherein M is a transition metal selected from Zr, Ti, Hf, V, No, Ta, Cr, Mo and W;

x is a valence of the transition metal;

L is a ligand coordinating to the transition metal and at least one of L is a ligand having a cyclopentadienyl skeleton selected from cyclopentadienyl, indenyl, 5,6,7,8-tetrahydroindenyl, 4,5,6,6a-tetrahydropentalenyl, 7,8-dihydro-3H,6H-as-indacenyl and fluorenyl, each of which may be substituted with a halogen, a hydrocarbon group, halogenated hydrocarbon group, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group; when there are two or more of the ligand having a cyclopentadienyl skeleton, two of them may be linked through a hydrocarbon group, a halogenated hydrocarbon group, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group; and L other than the ligand having a cyclopentadienyl skeleton is hydrogen, halogen, a hydrocarbon group, a halogenated hydrocarbon group, a silicon-containing group, an oxygen containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group).

10. The process as claimed in claim 6, wherein in the formula (III);

M^2 is Zr;

R^5, R^6, R^8, R^9 and R^{10} are each a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms;

R^7 is phenyl, α-naphthyl, β-naphthyl, anthracenyl, phenanthryl, pyrenyl, acenaphthyl, phenalenyl or aceanthlenyl,

Y^2 is a divalent hydrocarbon group of 1 to 20 carbon atoms, methylsilylene, dimethylsilylene, diethylsilylene, di(n-propyl)silylene, di(i-propyl)silylene, di(cyclohexyl)silylene, methylphenylsilylene, diphenylsilylene, di(p-tolyl)silylene, di(p-chlorophenyl)-silylene, tetramethyl-1,2-disilyl or tetraphenyl-1,2-disilyl; and

X^3 and X^4 are each a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a sulfonato or sulfinato group.

11. The process as claimed in claim 10, wherein the transition metal compound (A) is rac-dimethylsilyl-bis{1-(2-n-propyl-4-(9-phenanthryl)indenyl}zirconium dichloride or rac-dimethylsilyl-bis{1-(2-methyl-4-(phenyl)indenyl)}-zirconium dichloride.

12. The process as claimed in claim 5, 6, 9, 10 or 11, wherein the compound (B) is at least one member selected from

A

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the group consisting of:

(B-1) an organoaluminum compound of the formula:

$$R^9_nAlX_{3-n}$$

(wherein R^9 is a hydrocarbon group of 1 to 12 carbon atoms, X is a halogen or hydrogen atom, and n is 1 to 3), and

(B-2) an aluminoxane.

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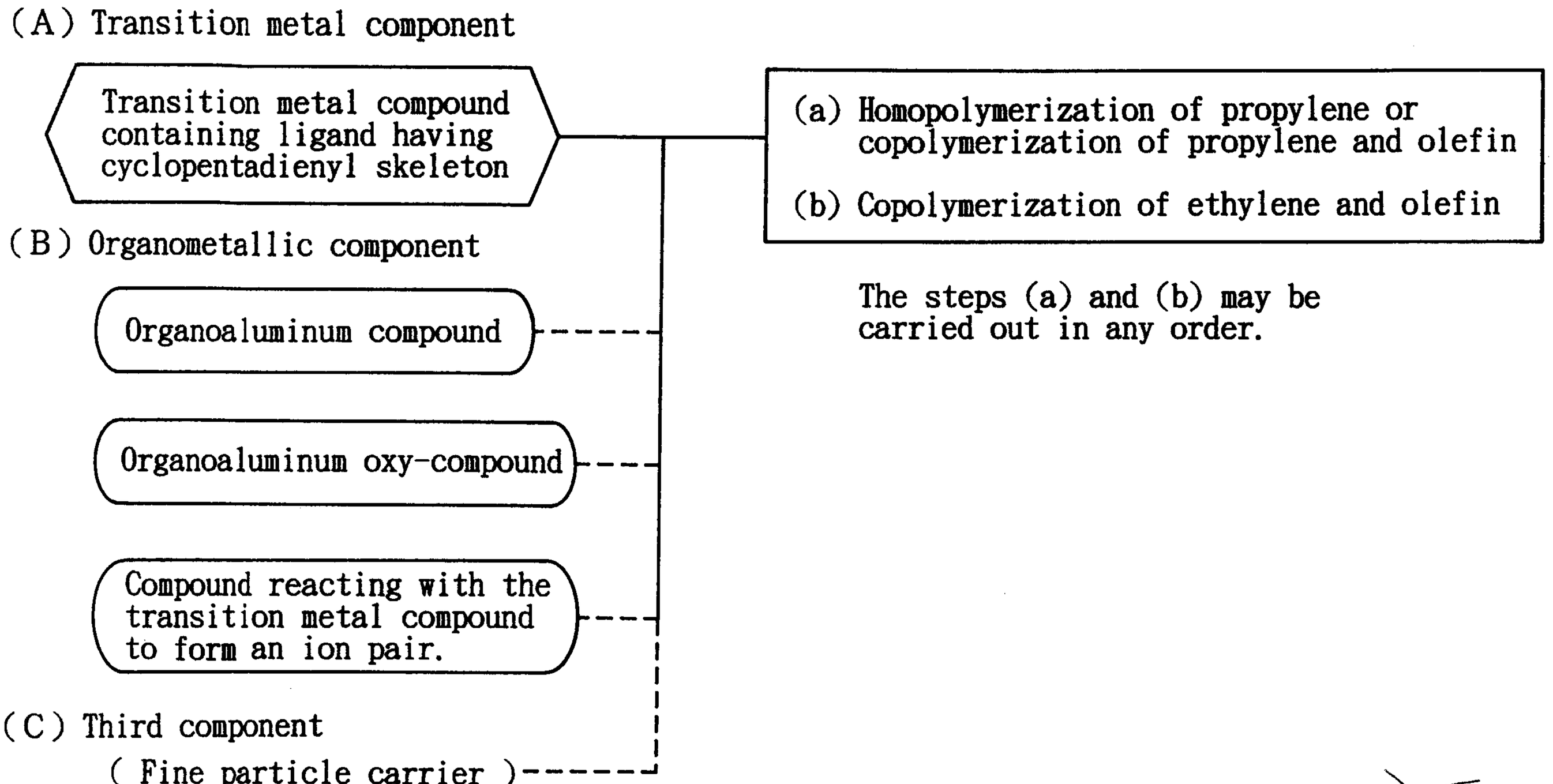
PATENT AGENTS

Fig. 1



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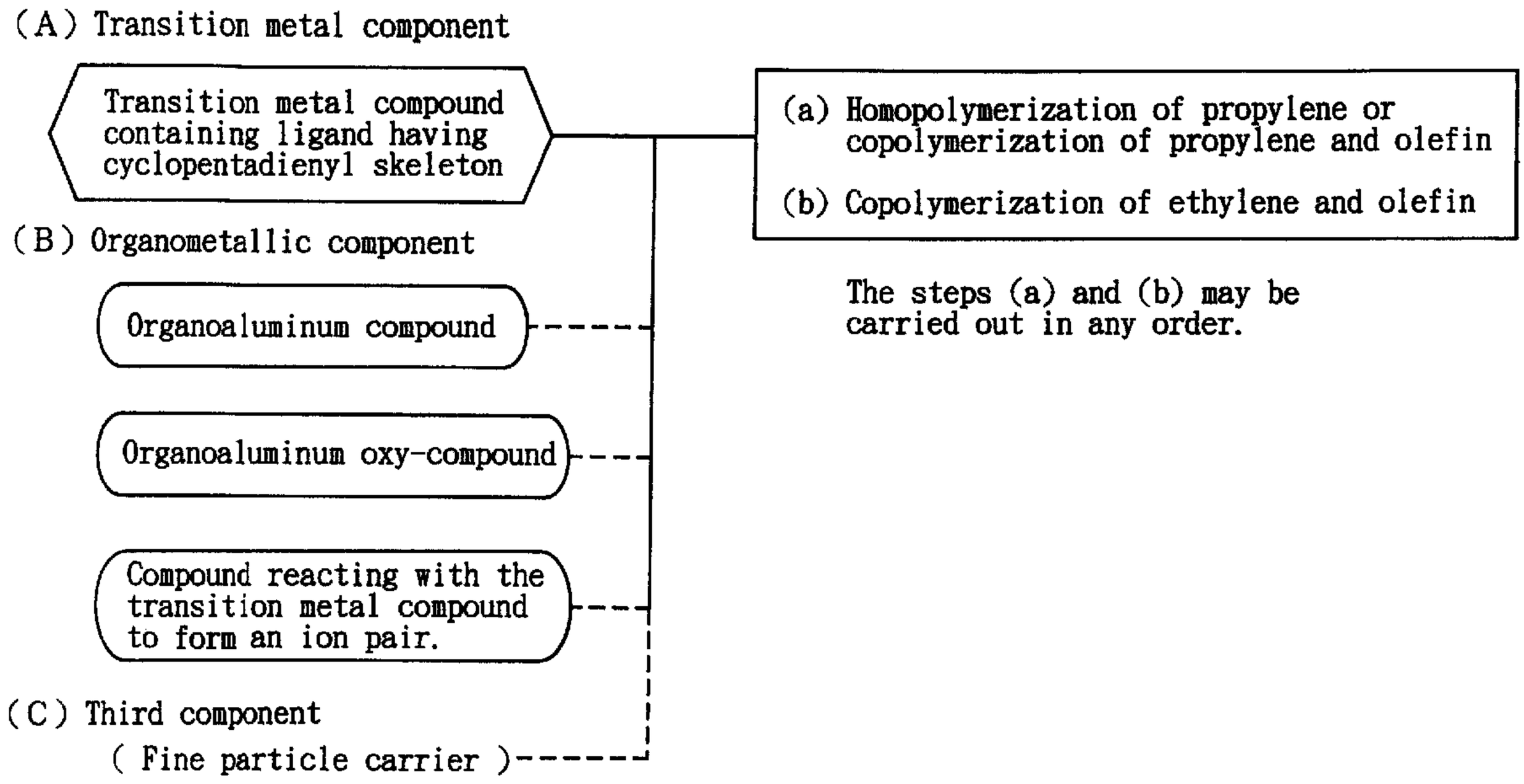
(A) Transition metal component
Transition metal compound containing ligand having cyclopentadienyl skeleton
(a) Homopolymerization of propylene or copolymerization of propylene and olefin
(b) Copolymerization of ethylene and olefin
The steps (a) and (b) may be carried out in any order.
(B) Organometallic component
Organoaluminum compound
Organoaluminum oxy-compound
Compound reacting with the transition metal compound to form an ion pair.
(C) Third component
(Fine particle carrier)