EXHIBIT V

PART 7

decane, and pouring the solution into a methanol/acetone (1/1) solution in an amount 5 times as much as that of decane to be precipitated is used as a sample to be measured. The measurement is carried out by extruding the sample at a resin temperature of 190° C., an extrusion rate of 10 mm/min and a take-up rate of 10 to 20 m/min using a MT measuring apparatus (manufactured by Toyo Seiki Seisakusho K. K.) having a nozzle diameter of 2.09 mm and a nozzle length of 8 mm. During the measurement of melt tension, the ethylene copolymer is premixed with 0.1% by weight of 2,6-di-tert-butyl-p-cresol as a crosslinking stabilizer.

Furthermore, in the ethylene copolymer of the invention, the temperature (T) at which its endothermic curve measured by a differential scanning calorimeter (DSC) shows the highest peak, and its density (d) satisfy the following relation:

$T < 400d - 250$, preferably

$T < 450d - 297$, more preferably

$T < 500d - 344$, particularly preferably

$T < 550d - 391$.

In addition, measurement by DSC was carried out using a DSC-7 type apparatus manufactured by Perkin Elmer Co., Ltd. The temperature (T) at which the endothermic curve shows the maximum peak is sought from an endothermic curve obtained by filling about 5 mg of a sample in an aluminum pan, heating to 200° C. at a rate of 10° C./min, holding the sample at 200° C. for 5 minutes, lowering the temperature to room temperature at a rate of 20° C./min, and then heating at a rate of 10° C./min.

In the ethylene copolymer of the invention, it is desirable that the quantity fraction (W) of a n-decane-soluble component and the density of the copolymer at 23° C. satisfy the following relation:

$\log W < -50d + 46.5$, preferably

$\log W < -50d + 46.4$, more preferably

$\log W < -50d + 46.3$.

It may be concluded from the relation between the temperature (T) and density (d), and the relation between the quantity fraction (W) of a n-decane-soluble component and density (d) that the ethylene copolymer of the present invention has a narrow composition distribution.

Moreover, the n-decane-soluble component quantity is obtained by a procedure described below.

Measurement of the n-decane-soluble component quantity (polymer having a smaller soluble component quantity has a narrower composition distribution) is carried out by adding 3 g of the copolymer to 450 ml of n-decane, dissolving the copolymer at 145° C., cooling the solution to 23° C., removing a n-decane-insoluble component by filtering, and recovering a n-decane-soluble component from the filtrate.

The ethylene copolymer according to the present invention having characteristics as described above can be prepared, for example, by copolymerizing ethylene with an α-olefin having 3 to 20 carbon atoms in the presence of a catalyst formed from

(i) a catalyst component obtained by the reaction of a bidentate compound in which two groups selected from negatively ionized indenyl groups or substituents thereof are bonded together through a group containing carbon and/or silicon such as a lower alkylene group and a halide of a transition metal in Group IVB of the periodic table, (the catalyst component is the substantially same as a transition metal compound comprising at least two ligands each having a cyclopentadienyl skelton, said at least two ligands being bonded together through a group containing carbon and/or silicon such as a lower alkylene group)

(ii) an organoaluminum oxy-compound,

(iii) an organoaluminum compound, and

(iv) a carrier, so that the thus obtained copolymer has a density of 0.86 to 0.95 g/cm^3.

In the catalyst component (i) in the invention, the bidentate compound (i—1) having two groups selected from negatively ionized indenyl groups or their substituents, which are bonded together through a group containing carbon and/or silicon such as a lower alkylene group, is represented by the formula

$$MR^1—R^2—R^3M$$

wherein R^1 and R^3 are each an indenyl anion, a substituted indenyl anion or a partially hydrogenated anion of either of these anions, R^1 and R^3 may be the same or different, R^2 is a lower alkylene group, and M is an alkali metal cation. Concrete examples of the bidentate compound (i—1) include ethylenebisindenylidilithium, ethylenebisindenylidisodium ethylenebis (4,5,6,7-tetrahydro-1-indenyl)dilithium, ethylenebis(4-methyl-1-indenyl)dilithium, ethylenebis(5-methyl-1-indenyl)dilithium, ethylenebis(6-methyl-1-indenyl)dilithium and ethylenebis(7-methyl-1-indenyl)dilithium.

Concrete examples of the halide (i-2) of a transition metal in Group IVB of the perodic table include zirconium tetrachloride, hafnium tetrachloride, titanium tetrachloride and titanium tetrabromide.

The catalyst component (i) of the invention is prepared by mixing and contacting such a bidentate compound as described above with such a transition metal compound and halide as described above in an organic solvent such as ether, tetrahydrofuran, benzene, toluene and methylene dichloride. During the preparation, the mixing molecular ratio ($MR^1—R^2—R^3M$/transition metal) of the bidentate compound (i-1) to the halide (i2) of a transition metal is 0.5 to 2, preferably 0.75 to 1.25, and the concentration of the transition metal is usually 0.03 to 0.5 mol/l, preferably 0.05 to 0.3 mol/l.

Next, the organoaluminum oxy-compound (ii) is explained below.

The organoaluminum oxy-compound (ii) may be a known aluminoxane or the benzene-insoluble organoaluminum oxy-compound having been discovered by the present inventors.

The above-mentioned aluminoxane may be prepared, for example, by the following procedures:

(1) a procedure for recovering an aluminoxane as its hydrocarbon solution which comprises adding an organoaluminum compound such as trialkylaluminum to a suspension in a hydrocarbon medium of a compound containing adsorbed water, or a salt containing water of crystallization such as magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate and cerous chloride hydrate, and reacting the organoaluminum compound; and

(2) a procedure for recovering an aluminoxane as its hydrocarbon solution which comprises reacting water, ice or steam directly with an organoaluminum compound such as trialkylaluminum in a solvent such as benzene, toluene, ethyl ether and tetrahydrofuran.

Moreover, the aluminoxane may contain a small amount of an organometal component. Furthermore, the solvent or unreacted organoaluminum compound may be removed from the above-mentioned recovered aluminoxane-containing solution, by distillation, and the aluminoxane may be redissolved in a solvent.

Concrete examples of the organoaluminum compound used for the preparation of the aluminoxane include

trialkylaluminum such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum, tridecylaluminum, 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 aryloxides such as diethylaluminum phenoxide.

Of these compounds, trialkylaluminum is particularly preferable.

Furthermore, there may also be used as the organoaluminum compound isoprenylaluminum represented by the general formula

$$(i\text{—}C_4H_9)_xAl_y(C_5H_{10})_z$$

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

The organoaluminum compounds mentioned above may be used either singly or in combination.

Solvents used for the solutions of the aluminoxane include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocrbons 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, kerosene and gas oil; and halogenated compounds derived from the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, especially chlorinated and brominated hydrocarbons.

In addition, there may also be used ethers such as ethyl ether and tetrahydrofuran. Of these solvents as exemplified above, aromatic hydrocarbons are particularly preferred.

The benzene-insoluble organoaluminum oxy-compounds used in the invention contain an Al component soluble in benzene at 60° C. in an amount of not greater than 10%, preferably not greater than 5%, particularly preferably not greater than 2% in terms of Al atom, and they are insoluble or sparingly soluble in benzene.

Solubility in benzene of such organoaluminum oxy-compounds as mentioned above is obtained by suspending in 100 ml of benzene the organoaluminum oxy-compound in an amount corresponding to 100 mg atoms in terms of Al, mixing the resulting suspension at 60° C. for 6 hours with stirring, filtering the resulting mixture with a G-5 glass filter equipped with a jacket kept at 60° C., washing 4 times the solid portion separated on the filter with 50 ml of benzene at 60° C., and measuring the amount (x mmole) of Al atoms present in the whole filtrate.

When the benzene-insoluble organoaluminum oxy-compounds as described above of the present invention are analyzed by infrared spectrophotometry (IR), a ratio (D_{1260}/D_{1220}) of an absorbance (D_{1260}) at about 1260 cm^{-1} to an absorbance (D_{1220}) at about 1220 cm^{-1} is preferably not greater than 0.09, more preferably not greater than 0.08, particularly preferably in the range of 0.04 to 0.07.

Infrared spectrophotometric analysis of the organoaluminum oxy-compounds is carried out in the following manner.

First, the organoaluminum oxy-compound is ground, together with nujol, in an agate mortar in a nitrogen box to form paste.

Next, the paste-like sample thus obtained is held between KBr plates, and IR spectrum is measured in a nitrogen atmosphere by means of IR-810 manufactured by Nippon Bunko K.K.

The IR spectrum of the organoaluminum oxy-compound used in the present invention is shown in FIG. 2.

From the thus obtained IR spectrum, a D_{1260}/D_{1220} ratio is sought, and a value of said ratio is obtained in the following manner.

(a) A line connecting a maximum point at about 1280 cm^{-1} and a maximum point at about 1240 cm^{-1} is taken as a base line L_1.

(b) A transmittance (T%) of an absorption minimum point at about 1260 cm^{-1} and a transmittance (T_O%) of a point of intersection formed by a vertical line from said absorption minimum point to a wave number axis (abscissa) and said base line L_1 are read, and an absorbance ($D_{1260}=\log T_O/T$) is calculated.

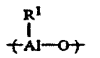
(c) Similarly, a line connecting maximum points at about 1280 cm^{-1} and at about 1180 cm^{-1} is taken as a base line L_2.

(d) A transmittance (T'%) of an absorption minimum point at about 1220 cm^{-1} and a transmittance (T'_O%) of a point of intersection formed by a vertical line from said absorption minimum point to a wave number axis (abscissa) and said base line L_2 are read, and an absorbance ($D_{1220}=\log T'_O/T'$) is calculated.

(e) From these values as obtained above, a D_{1260}/D_{1220} ratio is calculated.

The IR spectrum of a known benzene-soluble organoaluminum oxy-compound is shown in FIG. 3. As can be seen from FIG. 3, the benzene-soluble organoaluminum oxy-compound has a D_{1260}/D_{1220} value of about 0.10 to 0.13, and thus the benzene-insoluble organoaluminum oxy-compound of the present invention obviously differ from the known benzene-soluble organoaluminum oxy-compound on the value of D_{1260}/D_{1220}.

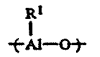
The benzene-insoluble organoaluminum oxy-compounds as described above are estimated to have an alkyloxyaluminum unit represented by the formula



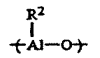
wherein R^1 is a hydrocarbon group of 1 to 12 carbon atoms.

In the above-mentioned alkyloxyaluminum unit, R^1 includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, octyl, decyl, cyclohexyl and cyclooctyl. Of these hydrocarbon groups exemplified above, preferred are methyl and ethyl, and particularly preferred is methyl.

In addition to the alkyloxyaluminum unit [I] of the formula



wherein R^1 is a hydrocarbon group of 1 to 12 carbon atoms, the benzene-insoluble organoaluminum oxy-compounds may contain an oxyaluminum unit [II] represented by the formula



wherein R^2 is a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy group of 1 to 12 carbon atoms, an aryloxy group of 6 to 20 carbon atoms, a hydroxyl group, halogen or hydrogen, provided that R^1 in the alkyloxyaluminum unit [I] and R^2 are different from each other. In that case, the organoaluminum oxy-compounds desirably contain the alkyloxyaluminum unit [I] in a proportion of not less than 30 mol %, preferably not less than 50 mol % particularly preferably not less than 70 mol %

The process for preparing the benzene-insoluble organoaluminum oxy-compounds as described above is concretely illustrated below.

The benzene-insoluble organoaluminum oxy-compound is obtained by bringing a solution of an aluminoxane into contact with water or an active hydrogen containing-compound.

Examples of the active hydrogen-containing compound include

- alcohols such as methanol, ethanol, n-propanol and isopropanol;
- diols such as ethylene glycol and hydroquinone; and
- organic acids such as acetic acid and propionic acid.

Of these compounds, preferred are alcohols and diols, and particulaly preferred are alcohols.

Water or the active hydrogen containing compound with which the solution of an aluminoxane is brought into contact may be used as a solution or a dispersions in a hydrocarbon solvent such as benzene, toluene and hexane, in an ether solvent such as tetrahydrofuran or in an amine solvent such as triethylamine, or may be used in the form of vapor or solid. The water with which the solution of an aluminoxane is brought into contact may be water of crystallization of a salt such as magnesium chloride, magnesium sulfate, aluminum sulfate, copper sulfate, nickel sulfate, iron sulfate and cerous chloride, or adsorbed water adsorbed to an inorganic compound such as silica, alumina and aluminum hydroxide or a polymer.

Reaction of an aluminoxane in a solution with water or an active hydrogen-containing compound is carried out usually in a solvent, for example, a hydrocarbon solvent. Examples of the solvent used in this case 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 methylcyclohexane;
- petroleum fractions such as gasoline, kerosene and gas oil; or halogenated compounds of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, particularly, chlorides and bromides; and ethers such as ethyl ether and tetrahydrofuran.

Of these solvents as exemplified above, particularly preferred are aromatic hydrocarbons.

In the reaction as mentioned above, water or the active hydrogen-containing compound is used in an amount of 0.1–5 moles, preferably 0.2–3 moles based on 1 g atom of Al present in the solution of an aluminoxane. The concentration in terms of aluminum atom in the reaction system is desirably 1×10^{-3}–5 gram atom/l, preferably 1×10^{-2}–3 gram atom/l, and the concentration of water in the reaction system is desirably 2×10^{-4}–5 mol/l, preferably 2×10^{-3}–3 mol/l.

The solution of an aluminoxane may be brought into contact with water or the active hydrogen-containing compound, for example, by the following procedures.

(1) A procedure which comprises bringing the solution of an aluminoxane into contact with a hydrocarbon solvent containing water or the active hydrogen-containing compound.

(2) A procedure which comprises blowing steam or the vapor of the active hydrogen-containing compound into the solution of an aluminoxane, thereby bringing the aluminoxane into contact with the steam or vapor.

(3) A procedure which comprises bringing the solution of an aluminoxane into contact directly with water, ice or the active hydrogen-containing compound.

(4) A procedure which comprises mixing the solution of an aluminoxane with a suspension of an adsorbed water-containing compound or a water of crystallization-containing compound in hydrocarbon, or with a suspension of a compound, to which the active hydrogen-containing compound is adsorbed, in hydrocarbon, thereby bringing the aluminoxane into contact with the adsorbed water or water of crystallization.

The solution of an aluminoxane may contain other components so long as they do not exert adverse effects on the reaction of the aluminoxane with water or the active hydrogen-containing compound.

The above-mentioned reaction of an aluminoxane in a solution with water or the active hydrogen-containing compound is carried out at a temperature of usually −50 to 150° C., preferably 0° to 120° C., more preferably 20° to 100° C. The reaction time employed is usually 0.5 to 300 hours, preferably about 1 to 150 hours, though said reaction time varies largely depending upon the reaction temperature used.

The benzene insoluble organoaluminum oxy-compound may also be prepared by direct contact of such

an organoaluminum as described above with water. In this case, water is used in such an amount that the organoaluminum atoms dissolved in the reaction system are not greater than 20% based on the total organoaluminum atoms.

Water with which the organoaluminum compound is brought into contact may be used as a solution or dispersion in a hydrocarbon solvent such as benzene, toluene and hexane, an ether solvent such as tetrahydrofuran or an amine solvent such as triethylamine, or may be used in the form of steam or ice. The water with which the organoaluminum compound is brought into contact may be water of crystallization of a salt such as magnesium chloride, magnesium sulfate, aluminum sulfate, copper sulfate, nickel sulfate, iron sulfate and cerous chloride, or adsorbed water adsorbed to an inorganic compound such as silica, alumina and aluminum hydroxide or a polymer.

Reaction of the organoaluminum compound with water is carried out usually in a solvent, for example, a hydrocarbon solvent. Examples of the solvent used in this case 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 methylcyclohexane;
- petroleum fractions such as gasoline, kerosene and gas oil; or halogenated compounds such as halides of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, particularly, chlorides and bromides; and ethers such as ethyl ether and tetrahydrofuran. Of these solvents as exemplified above, particularly preferred are aromatic hydrocarbons.

The concentration of the organoaluminum compound in the reaction system in terms of aluminum atom is desirably 1×10^{-3}–5 gram atom/l, preferably 1×10^{-2}–3 gram atom/l, and the concentration of water in the reaction system is desirably 1×10^{-3}–5 mol/l, preferably 1×10^{-2}–3 mol/l. In the reaction mentioned above, the organoaluminum atoms dissolved in the reaction system are not greater than 20%, preferably not greater than 10%, more preferably 0 to 5% based on the total organoaluminum atoms.

The organoaluminum compound may be brought into contact with water, for example, by the following procedures.

(1) A procedure which comprises bringing the hydrocarbon solution of the organoaluminum into contact with a hydrocarbon solvent containing water.

(2) A procedure which comprises blowing steam into the hydrocarbon solution of the organoaluminum, etc., thereby bringing the organoaluminum into contact with the steam.

(3) A procedure which comprises mixing the hydrocarbon solution of the organoaluminum with a suspension of an adsorbed water-containing compound or a water of crystallization-containing compound in hydrocarbon, thereby bringing the organoaluminum into contact with the adsorbed water or water of crystallization.

(4) A procedure which comprises bringing the hydrocarbon solution of the organoaluminum into contact directly with ice.

The hydrocarbon solution of the organoaluminum as described above may contain other components so long as they do not exert adverse effects on the reaction of the organoaluminum with water.

The above-mentioned reaction of the organoaluminum with water is carried out at a temperature of usually −100° to 150° C., preferably −70° to 100° C., more preferably at −50° to 80° C. The reaction time employed is usually 1 to 200 hours, preferably 2 to 100 hours, though the reaction time varies largely depending upon the reaction temperature used.

Next, the organoaluminum compound (iii) of the invention is illustrated below.

Examples of the organoaluminum compound (iii) used herein include an organoaluminum compound represented by the formula

$$R^6_nAlX_{3-n}$$

wherein R^6 is a hydrocarbon group of 1 to 12 carbon atoms, X is halogen or hydrogen, and n is 1 to 3.

In the above formula, R^6 is a hydrocarbon group of 1 to 12 carbon atoms, for example, an alkyl group, a cycloalkyl group or an aryl group. Concrete examples of R^6 include methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, cyclopentyl, cyclohexyl, phenyl and tolyl.

Concrete examples of such organoaluminum compounds include

- trialkylaluminum such as trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, trioctylaluminum and tri-2-ethylhexylaluminum;
- alkenylaluminum such as isoprenylaluminum;
- dialkylaluminum halides such as dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, diisobutylaluminum chloride and dimethylaluminum bromide;
- alkylaluminum sesquihalides such as methylaluminum sesquichloride, 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.

Furthermore, there may also be used other organoaluminum compounds represented by the formula

$$R^6_nAlY_{3-n}$$

wherein R^6 is as defined previously, Y is $—OR^7$, $—OSiR^8_3$, $—OAlR^9_2$, $—NR^{10}_2$, $—SiR^{11}_3$ or $—N(R^{12})AlR^{13}_2$, n is 1 to 2, R^7, R^8, R^9 and R^{13} are each methyl, ethyl, isopropyl, isobutyl, cyclohexyl or phenyl, R^{10} is hydrogen, methyl, ethyl, isopropyl, phenyl or trimethylsilyl, R^{11} and R^{12} are each methyl or ethyl.

The organoaluminum compounds as mentioned above include, in concrete, such compounds as enumerated below.

(1) Compounds of the formula $R^6_nAl(OR^7)_{3-n}$ such as dimethylaluminum methoxide, diethylaluminum ethoxide and diisobutylaluminum methoxide.

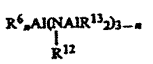
(2) Compounds of the formula $R^6_nAl(OSiR^8_3)_{3-n}$ such as $Et_2Al(OSiMe_3)$, $(iso\text{-}Bu)_2Al(OSiMe_3)$ and $(iso\text{-}Bu)_2Al(OSiEt_3)$.

(3) Compounds of the formula $R^6_nAl(OAlR^9_2)_{3-n}$ such as $Et_2AlOAlEt_2$ and $(iso\text{-}Bu)_2AlOAl(iso\text{-}Bu)_2$.

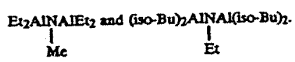
(4) Compounds of the formula $R^6_nAl(NR^{10}_2)_{3-n}$ such as Me_2AlNEt_2, $Et_2AlNHMe$, $Me_2AlNHEt$, $Et_2AlN(SiMe_3)_2$, $(iso\text{-}Bu)_2AlN(SiMe_3)_2$.

(5) Compounds of the formula $R^6_nAl(SiR^{11}_3)_{3-n}$ such as $(iso\text{-}Bu)_2AlSiMe_3$.

(6) Compounds of the formula



such as



Of the organoaluminum compounds as exemplified above, preferred are those having the formulas

R^6_3Al, $R^6_nAl(OR^7)_{3-n}$ and $R^6_nAl(OAlR^9_2)_{3-n}$

and particularly preferred are those having the above-mentioned formulas in which R^6 is isoalkyl and n is 2. These organoaluminum compounds may also be used in combination of two or more.

The carrier used as a carrier of the catalyst component (iv) of the invention is a solid inorganic or organic compound in granules or fine particles having a particle size of 10 to 300 μm, preferably 20 to 200 μm. Of these carriers, porous oxides are preferable as inorganic carriers. Concrete examples of the oxide carriers include SiO_2, Al_2O_3, MgO, ZrO_2, TiO_2, B_2O_3, CaO, ZnO, BaO, ThO_2, or a mixture of these compounds 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 carriers, preferred are those comprising at least one compound selected from the group consisting of SiO_2 and Al_2O_3 as a major component.

Furthermore, the above-mentioned inorganic oxide or oxides may also contain a small amount of a carbonate, a sulfate, a nitrate and an oxide such as 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 LiO_2.

Though the porous inorganic carriers have different properties among them depending on the types and preparation methods thereof, the carriers preferably used in the invention have a specific surface area of 50 to 1000 m^2/g, preferably 100 to 700 m^2/g, a pore volume of desirably 0.3 to 2.5 cm^2/g. The carriers are prepared if necessary by firing at a temperature of 150° to 1000° C., preferably 200° to 800° C.

Moreover, there can be mentioned organic compounds in solid granules or fine solid particles each having a particle size of 10 to 300 μm as carriers which can be used in the present invention. Examples of these organic compounds include (co)polymers containing as the main component constituent units derived from an α-olefin of 2 to 14 carbon atoms, such as ethylene, propylene, 1-butene and 4-methyl-1-pentene, or polymers or copolymers containing as the main component constituent units derived from vinylcyclohexane or styrene.

In the present invention, it is desirable that catalyst formed by prepolymerizing olefin on the catalyst components (i), (ii), (iii) and (iv) as described above should be used during the preparation of the ethylene copolymers.

Before the prepolymerization, the catalyst component (i), the catalyst components (i) and (ii), on the catalyst components (i), (ii) and (iii) may be supported on the catalyst component (iv), a carrier, or the catalyst components may only be arbitrarily contacted together and mixed, and used for the prepolymerization.

A sphere olefin copolymer excellent in particle shape can be manufactured if the catalyst component (i) is used, during the prepolymerization, with the transition metal compound (vi) comprising ligangs which have each a cyclopentadienyl skeleton and which are not bonded together.

Concrete examples of the transition metal compound (vi) comprising ligands which have a cyclopentadienyl skeleton and which are not bonded together include

bis(cyclopentadienyl)zirconium dichloride,
bis(methylcyclopentadienyl)zirconium dichloride,
bis(dimethylcyclopentadienyl)zirconium dichloride,
bis(ethylcyclopentadienyl)zirconium dichloride,
bis(n-butylcyclopentadienyl)zirconium dichloride, and
bis(indenyl)zirconium dichloride.

The proportion for use of the transition metal compound (vi) to the catalyst component (i) is 0 to 50 mol %, preferably 5 to 40 mol %, more preferably 10 to 30 mol % based on the total amount of the components (i) and (vi) defined as 100 mol %.

During the prepolymerization, the olefin polymer (v) is formed in an amount, based on 1 g of the carrier, of 0.05 to 100 g, preferably 0.1 to 50 g, more preferably 0.2 to 30 g.

Examples of the olefin include ethylene and an α-olefin having 3 to 20 carbon atoms, for example, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene. Of these, ethylene is preferable.

The prepolymerization is carried out without a solvent or in an inactive hydrocarbon solvent. In the prepolymerization process, there are used the organoaluminum compound in an amount of 0.2 to 20 mmoles, preferably 0.5 to 10 mmoles, the organoaluminum oxy-compound in an amount of 1 to 50 mg atoms, preferably 2 to 20 mg atoms in terms of Al, and the catalyst component (i) in an amount of 0.02 to 2 mg atoms, preferably 0.05 to 1 mg atom in terms of the transition metal, all the amounts being based on 1 g of the carrier.

Furthermore, a desirable molecular ratio of the orgnaoaluminum compound (iii) in terms of Al atom to the organoaluminum oxy-compound (ii) in terms of Al atom [Al (iii)/Al (ii)] is usually 0.02 to 3, preferably 0.05 to 1.5 A molecular ratio of the organoaluminum oxy-compound (ii) in terms of Al atom to the catalyst component (i) in terms of transition metal atom (M) [Al (ii)/M] is usually 5 to 250, preferably 10 to 150. When the prepolymerization is conducted in an inactive hydrocarbon solvent, the concentration of the catalyst component (i) in terms of the transition metal is usually 0.1 to 10 mg atom/liter, preferably 0.5 to 5 mg atom/-liter.

The prepolymerization is carried out at a temperature of −20° to 70° C., preferably −10° to 60° C., more preferably 0 to 50° C.

The prepolymerization may be carried out either batchwise or continuously, and under reduced pressure,

normal pressure or applied pressure. Though a molecular weight modifier such as hydrogen may be allowed to be present during prepolymerization, its amount is desirably restricted so that there can be prepared a prepolymer having an intrinsic viscosity [η] of not less than 0.2 dl/g, preferably 0.5 to 10 dl/g as measured in decalin at 135° C.

In the thus obtained prepolymerization catalyst, the catalyst component (i) is supported in an amount in terms of transition metal atom, based on 1 g of the carrier, of 0.1 to 50 rag, preferably 0.3 to 30 mg, more preferably 0.5 to 20 mg. The molecular ratio of the catalyst components (ii) and (iii) in terms of Al atom to the catalyst component (i) in terms of the transition metal (M) (Al/M) is 5 to 200, preferably 10 to 150, more preferably 15 to 100.

The ethylene copolymers according to the present invention are obtained by copolymerizing ethylene with such an α-olefin having 3 to 20 carbon atoms as propylene, 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.

In the present invention, olefin is usually polymerized in a gas phase or liquid phase, for example, in slurry. In the slurry polymerization, an inactive hydrocarbon or the olefin itself may be used as a solvent.

Concrete examples of the hydrocarbon solvent include aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzene, toluene and xylene; and petroleum fractions such as gasoline, kerosene and gas oil. Of these hydrocarbons, preferred are aliphatic hydrocarbons, alicyclic hydrocarbons and petroleum fractions.

In the present invention, the slurry polymerization is conducted at a temperature of usually −50° to 100° C., preferably 0° to 90° C.

In the present invention, the gas phase polymerization is carried out at a temperature of usually 0° to 120° C., preferably 20° to 100° C.

In the slurry polymerization or gas phase polymerization of the invention, the concentration of the transition metal compound is usually 10^{-8} to 10^{-2} g atom/liter, preferably 10^{-7} to 10^{-3} g atom/liter in terms of the transition metal.

Furthermore, in the polymerization of the invention, an aluminum oxy-compound or an aluminum compound similar to those used in the catalyst components (ii) and (iii) may be added. During the polymerization, the ratio of the aluminum compound in terms of Al atom to the transition metal atom (M) (Al/M) is 5 to 300, preferably 10 to 200, more preferably 15 to 150.

The polymerization is carried out usually at a normal pressure to 100 kg/cm^2, preferably under a pressure condition of 2 to 50 kg/cm^2. The polymerization can be carried out either batchwise, semicontinuously or continuously.

Furthermore, the polymerization may also be carried out in not less than 2 steps having reaction conditions different from each other.

The second process for the preparation of an olefin polymer according to the present invention is concretely illustrated below.

The olefin polymer, especially the ethylene polymer prepared by the second process for the preparation of an olefin polymer according to the present invention is an ethylene homopolymer or a random copolymer of ethylene with an α-olefin having 3 to 20 carbon atoms.

The random copolymer of ethylene with an α-olefin having 3 to 20 carbon atoms prepared by the second process for the preparation of an olefin polymer according to the present invention has characteristics as described above.

In the second process for the preparation of an olefin polymer of the invention, there is used a solid catalyst formed from

(A) a compound of a transition metal in Group IVB of the periodic table, having as a ligand at least two groups having a cyclopentadienyl skeleton, said at least two groups being crosslinked through a group containing carbon and/or silicon, and

(B) an organoaluminum oxy-compound, and polymerization of olefin is carried out under the condition that the produced polymer exists in a solid state in the polymerization system.

The transition metal compound (A) used in the second process for the preparation of an olefin polymer according to the present invention is represented by the formula

$$M^1L^1_x$$

wherein M^1 is a transition metal, L^1 is a ligand coordinating to the transition metal, at least two of L^1 are ligands having a cyclopentadienyl skeleton and bonded together through a group containing carbon and/or silicon, L^1 other than the ligand having a cyclopentadienyl skeleton is a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen, and x is a valence of the transition metal.

In the above-mentioned formula, M^1 is a transition metal, and concrete preferable examples of M^1 include zirconium, titanium, hafnium, chromium and vanadium. Of these, particularly preferred are zirconium and hafnium.

The ligands having a cyclopentadienyl skeleton include, for example, cyclopentadienyl, an alkyl-substituted cyclopentadienyl group such as methylcyclopentadienyl, ethylcyclopentadienyl, n-butylcyclopentadienyl, dimethylcyclopentadienyl and pentamethylcyclopentadienyl, indenyl, 4,5,6,7-tetrahydroindenyl and fluorenyl.

The ligand other than those having a cyclopentadienyl skeleton is a hydrocarbon group having 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen.

The hydrocarbon group having 1 to 12 carbon atoms includes, for example, an alkyl group, a cycloalkyl group, an aryl group and an aralkyl group, and concrete examples of these groups are as follows:

an alkyl group such as methyl, ethyl, propyl, isopropyl and butyl;

a cycloalkyl group such as cyclopentyl and cyclohexyl;

an aryl group such as phenyl and tolyl;

an aralkyl group such as benzyl and neophyl;

an alkoxy group such as methoxy, ethoxy and butoxy;

an aryloxy group such as phenoxy; and

halogen such as fluorine, chlorine, bromine and iodine.

Such a transition metal compound (A) comprising ligands having a cyclopentadienyl skeleton as used in the present invention and having a transition metal with

a valence of four may be represented more concretely by the formula

$$R^2R^3R^4R^5M^1$$

wherein M^1 is zirconium, titanium, hafnium or vanadium, at least two of R^2 R^3 R^4 and R^5 that is R^2 and R^3 are each a group having a cyclopentadienyl skeleton, said two groups, each having a cyclopentadienyl skeleton, being bonded together through a group containing carbon and/or silicon such as an alkylene group (e.g., ethylene and propylene), a substituted alkylene group such as isopropylidene and diphenylmethylene, a silylene group, and a substituted silylene group such as dimethylsilylene, R^4 and R^5 are each a group having a cyclopentadienyl skeleton, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, halogen or hydrogen.

Listed below are concrete examples of the transition metal compound (A) having at least two ligands containing a cyclopentadienyl skeleton, said at least two ligands having a cyclopentadienyl skeleton being bonded together through an alkylene group, a substituted alkylene group, a silylene group or a substituted silylene group.

Ethylenebis(indenyl)dimethylzirconium,
Ethylenebis(indenyl)diethylzirconium,
Ethylenebis(indenyl)diphenylzirconium monochloride,
Ethylenebis(indenyl)methylzirconium monochloride,
Ethylenebis(indenyl)ethylzirconium monochloride,
Ethylenebis(indenyl)methylzirconium monobromide,
Ethylenebis(indenyl)zirconium dichloride,
Ethylenebis(indenyl)zirconium dibromide,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethylzirconium,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methylzirconium monochloride,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride,
Ethylenebis(4,5, 6, 7-tetrahydro-1-indenyl)zirconium dibromide,
Ethylenebis(4-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(5-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(6-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(7-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(5-methoxy-1-indenyl)zirconium dichloride,
Ethylenebis(2,3-dimethyl-1-indenyl)zirconium dichloride,
Ethylenebis(4,7 -dimethyl-1-indenyl)zirconium dichloride,
Ethylenebis(4,7-dimethoxy-1-indenyl)zirconium dichloride,
Isopropylidene(cyclopentadienylfluorenyl)zirconium dichloride,
Isopropylidene(cyclopentadienyl-2,7-di-tert-butylfluorenyl)zirconium dichloride,
Isopropylidene(cyclopentadienylmethylcyclopentadienyl)zirconium dichloride,
Dimethylsilylenenbis(cyclopentadienyl)zirconium dichloride,
Dimethylsilylenebis(methylcyclopentadienyl)zirconium dichloride,
Dimethylsilylenenbis(dimethylcyclopentadienyl)zirconium dichloride,
Dimethylsilylenenbis(trimethylcyclopentadienyl)zirconium dichloride, and
Dimethylsilylenebis(indenyl)zirconium dichloride.

There may also be used transition metal compounds obtained by substituting titanium, hafnium or vanadium for zirconium in the above-exemplified zirconium compounds.

In the second process for the preparation of an olefin polymer according to the present invention, a compound similar to the organoaluminum oxy-compound (ii) is used as the organoaluminum oxy-compound (B).

Moreover, in the second process for the preparation of an olefin polymer according to the present invention, an organoaluminum compound (C) may also be used if necessary in addition to the transition metal compound (A) and the organoaluminum oxy-compound (B) as described above during the manufacture of olefin polymer.

A compound similar to the organoaluminum compound (iii) is used for such the organoaluminum compound (C).

The catalyst component used in the second process for the preparation of an olefin polymer according to the present invention is in a solid state, and such a solid catalyst component can be prepared, for example, by supporting the catalyst component (A) on a carrier (D) or a solid organoaluminum oxy-compound.

A carrier similar to that described above can be used as the carrier (D).

In the preparation of an ethylene polymer by the second process for the preparation of an olefin polymer according to the present invention, it is desirable that there should be used a catalyst formed by prepolymerizing olefin on catalyst components comprising the catalyst components (A) and (B), and if necessary the catalyst component (C) and/or the catalyst component (D), all these catalyst components having been described above.

Before the prepolymerization, the catalyst component (A), the catalyst components (A) and (B) or the catalyst components (A), (B) and (C) may be presupported on a carrier, or these catalyst components may only be arbitrarily contacted and mixed.

When a transition metal compound (E) containing ligands each having a cyclopentadienyl skeleton, said ligands being not bonded together, is used with the catalyst component (A) during contacting and mixing, a sphere olefin copolymer excellent in particle properties can be prepared.

The transition metal compound (E) used if necessary in the present invention is a compound similar to the above-described transition metal compound (vi) containing ligands each having a cyclopentadienyl skeleton, said ligands being not bonded together, and is illustrated more in detail below. The transition metal compound (E) is represented by the formula

$$M^2L^2_x$$

wherein M^2 is a transition metal, L^2 is a ligand coordinating to the transition metal, at least one of L^2 is a ligand having a cyclopentadienyl skeleton, L^2 other than the ligand having a cyclopentadienyl skeleton is a hydrocarbon group of 1 to 20 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen, and x is a valence of the transition metal.

In the above-mentioned formula, M^2 is a transition metal, and concrete preferable examples of M^2 include zirconium, titanium, hafnium, chromium and vanadium.

Of these, particularly preferred are zirconium and hafnium.

Examples of the ligand having a cyclopentadienyl skeleton include a cyclopentadienyl group an alkyl-substituted cyclopentadienyl group such as a methylcyclopentadienyl group, an ethylcyclopentadienyl group, a n-butylcyclopentadienyl group, a dimethylcyclopentadienyl group and a pentamethylcyclopentadienyl group, an indenyl group and a fluorenyl group.

At least one, preferably two ligands each having a cycloalkadienyl skeleton as mentioned above coordinate to the transition metal M^2.

The ligand other than those having a cycloalkadienyl skeleton is a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen.

The hydrocarbon group having 1 to 12 carbon atoms includes, for example, an alkyl group, a cycloalkyl group, an aryl group and an aralkyl group, and concrete examples of these groups are listed below.

The alkyl group includes methyl, ethyl, propyl, isopropyl and butyl.

The cycloalkyl group includes cyclopentyl and cyclohexyl.

The aryl group includes phenyl and tolyl.

The aralkyl group includes benzyl and neophyl.

The alkoxy group includes methoxy, ethoxy and butoxy.

The aryloxy group includes phenoxy.

The halogen includes fluorine, chlorine, bromine and iodine.

Such a transition metal compound (E) containing ligands each having a cyclopentadienyl skeleton, which is not bonded to other cyclopentadienyl skeletons, as used in the present invention and having a transition metal with a valence of 4 may be represented more concretely by the formula

$$R^{2'}kR^{3'}lR^{4'}mR^{5'}nM^2$$

wherein M^2 is zirconium, titanium, hafnium or vanadium, $R^{2'}$ is a group having a cyclopentadienyl skeleton, , $R^{3'}$, $R^{4'}$ and $R^{5'}$ are each a group having a cyclopentadienyl skeleton, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, halogen or hydrogen, k is an integer of not less than 1, and $k+l+m+n=4$.

Listed below are concrete examples of the transition metal compound (E) having zirconium as M^2 and ligands each containing a cyclopentadienyl skeleton which is not bonded to other cyclopentadienyl skeletons.

Bis(cyclopentadienyl)zirconium monochloride monohydride,
Bis(cyclopentadienyl)zirconium monobromide monohydride,
Bis(cyclopentadienyl)methylzirconium hydride,
Bis(cyclopentadienyl)ethylzirconium hydride,
Bis(cyclopentadienyl)phenylzirconium hydride,
Bis(cyclopentadienyl)benzylzirconium hydride,
Bis(cyclopentadienyl)neopentylzirconium hydride,
Bis(methylcyclopentadienyl)zirconium monochloride hydride,
Bis(indenyl)zirconium monochloride monohydride,
Bis(cyclopentadienyl)zirconium dichloride,
Bis(cyclopentadienyl)zirconium dibromide,
Bis(cyclopentadienyl)methylzirconium monochloride,
Bis(cyclopentadienyl)ethylzirconium monochloride,
Bis(cyclopentadienyl)cyclohexylzirconium monochloride,
Bis(cyclopentadienyl)phenylzirconium monochloride,
Bis(cyclopentadienyl)benzylzirconium monochloride,
Bis(methylcyclopentadienyl)zirconium dichloride,
Bis(dimethylcyclopentadienyl)zirconium dichloride,
Bis(n-butylcyclopentadienyl)zirconium dichloride,
Bis(indenyl)zirconium dichloride,
Bis(indenyl)zirconium dibromide,
Bis(cyclopentadienyl)zirconiumdimethyl,
Bis(cyclopentadienyl)zirconiumdiphenyl,
Bis(cyclopentadienyl)zirconiumdibenzyl,
Bis(cyclopentadienyl)zirconium methoxychloride,
Bis(cyclopentadienyl)zirconium ethoxychloride,
Bis(methylcyclopentadienyl)zirconium ethoxychloride,
Bis(cyclopentadienyl)zirconium phenoxychloride, and
Bis(fluorenyl)zirconium dichloride.

There may also be used transition metal compounds obtained by substituting titanium, hafnium or vanadium for zirconium in the above-exemplified zirconium compounds.

During the prepolymerization, the olefin polymer is formed in an amount, based on 1 g of the carrier, of 0.05 to 100 g, preferably 0.1 to 50 g, more preferably 0.2 to 30 g.

Examples of the olefin include ethylene and an α-olefin having 3 to 20 carbon atoms, for example, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene. Of these, ethylene is preferable.

The prepolymerization is carried out without a solvent or in an inactive hydrocarbon solvent. During the prepolymerization, there are used the organoaluminum compound in an amount of 0.2 to 20 mmoles, preferably 0.5 to 10 mmoles, the organoaluminum oxy-compound in an amount of 1 to 50 mg atoms, preferably 2 to 20 mg atoms in terms of Al, and the catalyst component (A) in an amount of 0.02 to 2 mg atoms, preferably 0.05 to 1 mg atom in terms of the transition metal, all the amounts being based on 1 g of the carrier.

Furthermore, a desirable molecular ratio [Al(C)/Al(B)] of the orgnaoaluminum compound in terms of Al atom [Al(C)] to the organoaluminum oxy-compound in terms of Al atom [Al(B)] is usually 0.02 to 3, preferably 0.05 to 1.5. A desirable molecular ratio [Al(B)/M] of the organoaluminum oxy-compound in terms of Al atom [Al(B)] to the catalyst component (A) in terms of transition metal atom (M) is usually 5 to 250, preferably 10 to 150. When the prepolymerization is carried out in an inactive hydrocarbon solvent, the concentration of the catalyst component (A) in terms of the transition metal atom is usually 0.1 to 10 mg atom/l, preferably 0.5 to 5 mg atom/l.

The prepolymerization is carried out at a temperature of $-20°$ to $70°$ C., preferably $-10°$ to $60°$ C., more preferably $0°$ to $50°$ C.

The prepolymerization may be carried out either batchwise or continuously, and under reduced pressure, normal pressure or applied pressure. Though a molecular weight modifier such as hydrogen may be allowed to be present during prepolymerization, its amount is desirably restricted so that there can be prepared a prepolymer having an intrinsic viscosity [η] of not less than 0.2 dl/g, preferably 0.5 to 10 dl/g as measured in decalin at 135° C.

In the thus obtained prepolymerization catalyst, the catalyst component (A) is supported in an amount in terms of transition metal atom, based on 1 g of the carrier, of 0.1 to 50 mg, preferably 0.3 to 30 mg, more preferably 0.5 to 20 mg. A molecular ratio (Al/M) of the catalyst components (B) and (C) in terms of Al atom to the catalyst component (A) in terms of the transition metal (M) is 5 to 200, preferably 10 to 150, more preferably 15 to 100.

The ethylene copolymers according to the present invention are obtained by copolymerizing ethylene with such an α-olefin having 3 to 20 carbon atoms as propylene, 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.

In the second process for olefin polymerization according to the present invention, olefin is usually polymerized under the condition that the produced polymer exists in a solid state, for example in a gas phase or in slurry. In the slurry polymerization, an inactive hydrocarbon or the olefin itself may be used as a solvent.

Concrete examples of the hydrocarbon solvent include

aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane;

alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane;

aromatic hydrocarbons such as benzene, toluene and xylene; and

petroleum fractions such as gasoline, kerosene and gas oil. Of these hydrocarbons, preferred are aliphatic hydrocarbons, alicyclic hydrocarbons and petroleum fractions.

In the present invention, the slurry polymerization is carried out at a temperature of usually −50° to 100° C. preferably 0° to 90° C.

In the present invention, the gas phase polymerization is carried out at a temperature of usually 0° to 120° C., preferably 20° to 100° C.

In the slurry polymerization or gas phase polymerization of the invention, the concentration of the transition metal in the polymerization reaction system is usually 10^{-8} to 10^{-2} g atom/l, preferably 10^{-7} to 10^{-3} g atom/l.

Furthermore, in the polymerization of the invention, an aluminum oxy-compound or an aluminum compound similar to those used in the preparation of the catalyst components (B) and (C) may be added to the reaction system. During the polymerization, a ratio (Al/M) of the aluminum compound in terms of Al atom to the transition metal atom (M) (Al/M) is 5 to 300, preferably 10 to 200, more preferably 15 to 150.

The polymerization is carried out usually at a normal pressure to 100 kg/cm² preferably under an applied pressure condition of 2 to 50 kg/cm². The polymerization can be carried out either batchwise, semicontinuously or continuously.

Furthermore, the polymerization may also be carried out in not less than 2 steps having reaction conditions different from each other.

The solid catalyst for olefin polymerization of the present invention is illustrated below.

The first prepolymerized solid catalyst for olefin polymerization according to the present invention is formed by prepolymerizing olefin in a suspension or a gas phase in the presence of a solid catalyst comprising

[A] a fine particle carrier,

[B] a transition metal compound (designated as a nonbridge type transition metal compound hereinafter) comprising ligands having a cyclopentadienyl skeleton, the cyclopentadienyl skeletons being not bonded mutually,

[C] a transition metal compound (designated as a bridge type transition metal compound) comprising at least two ligands each having a cyclopentadienyl skeleton, said at least two ligands being bonded together through an alkylene group, a substituted alkylene group, a silylene group or a substituted silylene group, and

[D] an organoaluminum oxy-compound.

The second prepolymerized solid catalyst for olefin polymerization according to the present invention is formed from the above-described components [A], [B], [C], [D], and [E] an organoaluminum compound.

The above-described carrier (iv) is used as the fine particle carrier [A].

There can be used as the nonbridge type transition metal compound [B] the same compound as the transition metal compound (E) described above comprising ligands having a cyclopentadienyl skeleton, the cyclopentadienyl skeletons being not bonded mutually.

There can be used as the bridge type transition metal compound [C] the same compound as described above.

Furthermore, the same compound as described above is used as the organoaluminum oxy-compound [D].

Still furthermore, the same compound as described above is used as the organoaluminum compound [E].

The prepolymerized solid catalyst for olefin polymerization of the invention is prepared by mixing the fine particle carrier [A], the nonbridge type transition metal compound [B], the bridge type transition metal compound [C], the organoaluminum oxy-compound [D] and if necessary the organoaluminum compound [E] in an inactive hydrocarbon solvent, and introducing olefin for prepolymerization.

Though the mixing may be conducted in an arbitrarily selected order, the mixing and contacting is preferably conducted in the order of [A]→([E])→[D]→[B]→olefin→[C]→olefin, or [A]→([E])→[D]→olefin.

The prepolymerized solid catalyst for olefin polymerization of the invention may also be prepared by supporting the nonbridge type transition metal compound [B], the bridge type transition metal compound [C], the organoaluminum compound [D] and if necessary the organoaluminum compound [E] on the fine particle carrier [A], introducing olefin without a solvent, and carrying out prepolymerization.

When the components [A] to [D], and if necessary the component [E] are mixed, the component [B] and the component [C] are used in the total amount of usually 10^{-5} to 5×10^{-3} mol, preferably 5×10^{-5} to 10^{-3} mol based on 1 g of the component [A], and in the total concentration of about 10^{-4} to 2×10^{-2} mol/l, preferably 2×10^{-4} to 10^{-2} mol/l. The component [B] is used in an amount of 5 to 80 mol % preferably 7 to 70 mol %, more preferably 10 to 60 mol % based on the amount of the component [B] and the component [C] of 100 mol % in total.

The atomic ratio [Al/(transition metal)] of the aluminum in the component [D] to the transition metal in the components [B] and [C] is usually 10 to 500, preferably 20 to 200. The atomic ratio (Al_E/Al_D) Of the aluminum atoms (AL_E) in the component [E] used if necessary to the aluminum atoms (Al_D) in the component [D] is usually 0.02 to 3, preferably 0.05 to 1.5. The compo-

nents [A] to [D], and if necessary the component [E] are mixed at a temperature of usually −20° to 80° C., preferably 0° to 60° C., with a contact time of 1 to 200 minutes, preferably 5 to 120 minutes.

Olefin is prepolymerized in the presence of the components [A] to [D], and if necessary the component [E], described above. The prepolymerization is carried out with the transition metal compounds used in an amount of usually 10^{-4} to 2×10^{-2} mol/l, preferably 5×10^{-4} to 10^{-2} mol/l, at a temperature of −20° to 80° C., preferably 0° to 50° C., and for a period of 0.5 to 100 hours, preferably 1 to 50 hours.

Though olefin used in the prepolymerization is selected from the olefin used in the polymerization, ethylene is preferable.

In the prepolymerized solid catalyst for olefin polymerization of the invention obtained as described above, the transition metal is supported in an amount of 5×10^{-6} to 5×10^{-4} g atom, preferably 10^{-5} to 3×10^{-4} g atom, and aluminum is supported in an amount of 10^{-3} to 10^{-1} g atom, preferably 2×10^{-3} to 5×10^{-2} g atom, all the amounts being based on 1 g of the component [A].

Furthermore, the polymer is formed during the prepolymerization in an amount, based on 1 g of the fine particle carrier, of about 0.1 to 500 g, preferably 0.3 to 300 g, particularly preferably 1 to 100 g.

Concrete examples of the inactive hydrocarbon used as a solvent for the preparation of the solid catalyst for olefin polymerization of the invention include

- aliphatic hydrocarons such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosene;
- alicyclic hydrocarbons such as cyclopentane, cyclohexane and methylcyclopentane;
- aromatic hydrocarbons such as benzene, toluene and xylene;
- halogenized hydrocarbons such as ethylene chloride, chlorobenzene and dichloromethane; and
- mixtures of these hydrocarbons.

In the polymerization of olefin with such the prepolymerized solid catalyst for olefin polymerization having a prepolymerized olefin as described above, the transition metal compounds [B] and [C] are desirably used in an amount (per liter of the polymerization volume) of usually 10^{-8} to 10^{-3} g atom, preferably 10^{-7} to 10^{-4} g atom in terms of the transition metal. In the polymerization, an organoaluminum compound and an aluminoxane may be used if necessary. Examples of the organoaluminum compound used in the polymerization include compounds similar to the organoaluminum compound [E] described above. The organoaluminum compound is used in an amount of 0 to 500 moles, preferably 5 to 200 moles based on 1 g atom of the transition metal.

The olefins which can be polymerized with such the prepolymerized catalyst for olefin polymerization include ethylene and α-olefins each having 3 to 20 carbon atoms, for example, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene. In addition, styrene, vinylcyclohexane and dienes may also be employed.

In the present invention, the polymerization can be practiced either by a process for liquid phase polymerization such as solution polymerization and suspension polymerization, or by a process for gas phase polymerization.

In the process for liquid phase polymerization, the same inactive hydrocarbon solvent as employed in the catalyst preparation can be used, and the olefin itself can also be used as a solvent.

The olefin polymerization is carried out with such a catalyst as described above for olefin polymerization at a temperature of usually −50° to 150° C., preferably 0° to 100° C., at a pressure of usually a normal pressure to 100 kg/cm², preferably a normal pressure to 50 kg/cm². The polymerization reaction can be carried out either batchwise, semicontinuously or continuously. Moreover, the polymerization may also be carried out in two or more steps having reaction conditions different from each other. The molecular weight of the produced olefin polymer can be adjusted either by placing hydrogen in the polymerization system, or by changing the polymerization temperature.

Furthermore, in the present invention, the catalyst for olefin polymerization may also contain components which are different from the above-mentioned components and which are useful for olefin polymerization.

The present invention is illustrated below with reference to examples, but it should be construed that the present invention is in no way limited to those examples.

In addition, the melt tension (abbreviated to MT sometimes hereinafter) in this specification is measured by a procedure described below.

The melt tension (MT) is determined by measuring the stress of a molten polymer while the polymer is being stretched at a constant rate. That is, there are used as samples for measurement fine particles of a produced polymer or a polymer obtained by dissolving the fine particles in decane once, and precipitating the dissolved powder with a methanol/acetone (volume ratio of 1/1) solution in a volume amount of not less than 5 times as much as that of decane, and the measurement was carried out using a MT measuring apparatus (manufactured by Toyoseiki Seisakusho K.K.) having a nozzle diameter of 2.09 mm and a nozzle length of 8 mm at a resin temperature of 190° C., an extrusion rate of 10 mm/min and a take-up speed of 10 to 20 m/min.

During measurement of the melt tension, ethylene copolymer samples are premixed with 0.1% by weight of 2,6-di-tert-butyl-p-cresol, a crosslinking stabilizer.

EXAMPLE 1

[Preparation of a catalyst component (A)]

A 400 ml glass flask purged with nitrogen was charged with 20 g of bis(indenyl)ethane and 200 ml of THF. The contents were cooled to −50° C. with stirring, and 100 ml of a solution of n-BuLi (1.6M solution) was added over a period of 50 minutes. Successively, the resultant mixture was stirred at −50° C. for 1 hour, and allowed to stand to be warmed to room temperature, whereby bis(indenyl)ethane became anionic. To the contents were added 100 ml of THF to form a homogeneous solution.

Another 1 liter glass flask purged with nitrogen was charged with 250 ml of THF, cooled to −50° C., and 16.54 g of zirconium tetrachloride was gradually added. The contents were warmed to 60° C., and stirred for 1 hour The anionic ligand prepared above was added dropwise. The resultant mixture was stirred at 60° C. for 3 hours, and filtered with a glass filter. The filtrate was condensed to 1/5 of the initial volume at room

temperature to precipitate a solid, which was separated by filtering with a glass filter, and the solid residue was washed with a hexane/ether (volume ratio of 1/1) solvent mixture, and dried under reduced pressure to obtain a catalyst component (A).

[Preparation of a catalyst component (B)]

A 400 ml flask thoroughly purged with nitrogen was charged with 37 g of $Al_2(SO_4)_3 \cdot 14H_2O$ and 125 ml of toluene. The contents were cooled to 0° C., and 500 mmoles of trimethylaluminum diluted with 125 ml of toluene was added dropwise. The resultant mixture was warmed to 40° C., and the reaction was continued at the temperature for 48 hours. After the completion of the reaction, the reaction mixture was subjected to solid-liquid separation by filtering, and toluene was removed from the filtrate, whereby 9.1 g of a white solid catalyst component (B) was obtained.

[Preparation of a prepolymerized catalyst]

A 400 ml flask thoroughly purged with nitrogen was charged with 1.29 g of silica (F-948, from Fuji Davison K.K.) which was fired at 700° C. for 6 hours before charging and 20 ml of toluene to form a suspension. To the suspension was added 4.51 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes. Successively, 7.91 ml of a toluene solution of the catalyst component (B) prepared above (Al: 0.95 mole/liter) was added, and the mixture was stirred at room temperature for 30 minutes. Then, 72 ml of a toluene solution of the catalyst component (A) prepared above (Zr: 0.00298 mole/liter) was added, and the resultant mixture was stirred for 10 minutes. Then, 52 ml of decane was further added, and prepolymerized was carried out at 30° C. for 4 hours by continuously introducing ethylene at a normal pressure.

After the completion of the prepolymerization, the solvent was removed by decantation, and the residue was washed at 50° C. three times with 200 ml of hexane, and further washed at room temperature three times with 200 ml of hexane, whereby there was obtained a prepolymerized catalyst containing 8.5 mg of Zr, 160 mg of Al and 15 g of polyethylene based on 1 g of silica.

[Polymerization]

A stainless steel autoclave having a content volume of 2 liter and thoroughly purged with nitrogen was charged with 150 g of sodium chloride (special grade, from Wako Junyaku K.K.), and the contents were dried for 1 hour at 90° C. under reduced pressure. Thereafter, the system pressure was returned to a normal pressure by introducing a gas mixture of ethylene and 1-butene (1-butene content: 6.3 mol %), and the system temperature was lowered to 70° C.

To the autoclave was added the prepolymerized catalyst prepared above in an amount of 0.0075 mg atom in terms of zirconium and 1.13 mmoles of triisobutylaluminum.

Thereafter, 50 Nml of hydrogen and the gas mixture of ethylene and 1-butene described above were successively introduced, and polymerization reaction was started at the total pressure of 4 kg/cm^2-G, whereby the system temperature immediately rose to 80° C. Thereafter, the polymerization was carried out at 80° C. for 1 hour while the total pressure was being maintained at 4 kg/cm^2-G by feeding only the gas mixture.

After the completion of the polymerization, sodium chloride was removed from the reaction mixture by washing with water, and the remaining polymer was washed with methanol and dried overnight at 80° C. under reduced pressure, whereby there was obtained 116 g of an ethylene/1-butene copolymer containing 8.1% by weight of 1-butene constituent units and 2.8% by weight of a decane-soluble component at 23° C. having a MFR of 2.30 g/10 min measured at 190° C. and a load of 2.16 kg, a density of 0.915 g/cm^3, a melt tension (MT) of 5.3 g and a bulk specific gravity of 0.31 g/cm^3, and showing an endothermic curve having the maximum peak at 94° C. when measured by a differential scanning calorimeter (DSC).

EXAMPLE 2

[Preparation of a prepolymerized catalyst]

To 1.30 g of the same silica as used in Example 1 was added 20 ml of decane to form a suspension. To the suspension was added 3.24 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 17.1 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 1.03 ml of a toluene solution of bis(cyclopentadienyl)zirconium dichloride (Zr: 0.0417 mole/liter), and the resultant mixture was stirred for 15 minutes. To the mixture was added 50 ml of decane, and prepolymerization was carried out at 30° C. for 2 hours by continuously introducing ethylene at a normal pressure. Thereafter, 100.5 ml of a toluene solution of the catalyst component (A) containing 0.00172 mole/liter of Zr, and the prepolymerization was continued at 30° C. for 4 hours. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 9.3 mg of zirconium, 190 mg of aluminum and 20 g of polyethylene.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that there were used a gas mixture containing 3.6 mol % of 1-butene, 10 Nml of hydrogen and the above-described prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out at 70° C. for 2 hours, whereby there was obtained 88 g of an ethylene/1-butene copolymer containing 6.7% by weight of 1-butene constituent units and 0.25% by weight of a decane-soluble component, having a MFR of 0.48 g/10 min, a density of 0.922 g/cm^3, a melt tension of 11 g and a bulk specific gravity of 0.35 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 103° C.

EXAMPLE 3

[Preparation of a prepolymerized catalyst]

To 3.0 g of the same silica as used in Example 1 was added 30 ml of decane to form a suspension. To the suspension was added 7.45 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 25 minutes.

Then, to the suspension was added 39.4 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 2.14 ml of a toluene solution of bis (methylcyclopentadienyl) zirco-

nium dichloride (Zr: 0.0465 mole/liter), and the resultant mixture was stirred for 10 minutes. To the mixture was added 100 ml of decane, and prepolymerization was carried out at 25° C. for 2.5 hours by continuously introducing ethylene at a normal pressure.

Thereafter, 166.4 ml of a toluene solution of the catalyst component (A) containing 0.00240 mole/liter of Zr, and the prepolymerization was continued at 30° C. for 5 hours. A subsequent procedure similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 8.2 mg of zirconium, 150 mg of aluminum and 20 g of polyethylene.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that 30 Nml of hydrogen was added, and that the prepolymerization catalyst described above was used, whereby there was obtained 149 g of an ethylene/1-butene copolymer containing 10.1% by weight of 1-butene constituent units and 3.1% by weight of a decane-soluble component, and having a MFR of 1.78 g/10 min, a density of 0.912 g/cm^3, a melt tension of 5.3 g and a bulk specific gravity of 0.36 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 94° C.

EXAMPLE 4

[Preparation of a prepolymerized catalyst]

To 1.49 g of the same silica as used in Example 1 was added 25 ml of decane to form a suspension. To the suspension was added 3.72 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 45 minutes.

Then, to the suspension was added 19.6 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 45 minutes.

Thereafter, to the suspension was added 2.13 ml of a toluene solution of bis (methylcyclopentadienyl) zirconium dichloride (Zr: 0.0465 mole/liter), and the resultant mixture was stirred for 10 minutes. To the mixture was further added 75 ml of decane, and prepolymerization was carried out at 30° C. for 1.5 hours by continuously introducing ethylene at a normal pressure.

Thereafter, to the reaction mixture was added 51.9 ml of the toluene solution of the catalyst component (A) containing 0.00287 mole/liter of Zr and prepared in Example 1, and prepolymerization was continued at 30° C. for 4 hours. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 10.5 mg of zirconium, 190 mg of aluminum and 17 g of polyethylene based on 1 g of silica.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that there were used a gas mixture containing 4.4 mol % of 1-butene, 30 Nml of hydrogen and the above-described prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.5 mmole in terms of triisobutylaluminum, whereby there was obtained 48 g of an ethylene/1-butene copolymer containing 6.5% by weight of 1-butene constituent units and 0.32% by weight of a decane-soluble component, having a MFR of 3.1 g/10 min, a density of 0.922 g/cm^3, a melt tension of 4.9 g and a bulk specific gravity of 0.36 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 115° C.

EXAMPLE 5

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that there were used a gas mixture containing 3.6 mol % of 1-butene, 30 Nml of hydrogen and the prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out at 70° C. for 1 hour, whereby there was obtained 95 g of an ethylene/1-butene copolymer containing 7.4% by weight of 1-butene constituent units and 0.18% by weight of a decane-soluble component, having a MFR of 0.075 g/10 min, a density of 0.920 g/cm^3 a melt tension of 42 g and a bulk specific gravity of 0.24 g/cm^3 and showing an endothermic curve (measured by DSC) with the maximum peak at 103° C.

Comparative Example 1

[Preparation of a prepolymerized catalyst]

To 3.14 g of the same silica as used in Example 1 was added 25 ml of decane to form a suspension, and 13.1 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter) was added to the suspension. The resultant mixture was stirred at room temperature for 45 minutes.

Then, to the suspension was added 36.5 ml of a toluene solution of an organoaluminum oxy-compound (Al: 1.79 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 20 minutes.

Thereafter, to the suspension was added 10.9 ml of a toluene solution of bis(methylcyclopentadienyl)zirconium dichloride (Zr: 0.0480 mole/liter), and the resultant mixture was stirred for 30 minutes. To the mixture was further added 100 ml of decane, and prepolymerization was carried out at 30° C. for 4.5 hours by continuously introducing ethylene at a normal pressure. A subsequent washing operation similar to that of Example 1 was conducted to obtain a prepolymerization catalyst containing 7.6 mg of zirconium, 190 mg of aluminum and 9.7 g of polyethylene based on 1 g of silica.

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there were used a gas mixture containing 6.1 mol % of 1-butene and the above-described prepolymerized catalyst in an amount of 0.015 mg atom in terms of zirconium and 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm^2-G, whereby there was obtained 137 g of an ethylene/1-butene copolymer containing 7.2% by weight of 1-butene constituent units and 1.1% by weight of a decane-soluble component, having a MFR of 1.29 g/10 min, a density of 0.920 g/cm^3, a melt tension of 1.9 g and a bulk specific gravity of 0.37 g/cm^3, and showing an endothermic curve (measured by DSC) with the maximum peak at 114° C.

EXAMPLE 6

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there was used a polymerization catalyst in an amount of 0.003 mg atom in terms of zirconium and 0.54 mmole in terms of triisobutylaluminum, and that polymerization of only ethyl-

ene was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm²-G, whereby there was obtained 121 g of an ethylene polymer having a MFR of 0.29 g/10 min, a melt tension of 17.5 g and a bulk specific gravity of 0.32 g/cm³.

EXAMPLE 7

[Polymerization]

A procedure similar to that of Example 3 was repeated except that there were used a gas mixture containing 3.9 mol % of 1-butene, 50 Nml of hydrogen and the prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium and 0.5 mmole in terms of triisobutylaluminum, and that polymerization was carried out at the total pressure of 2.5 kg/cm²-G, whereby there was obtained 119 g of an ethylene/1-butene copolymer containing 7.0% by weight of 1-butene constituent units and 0.35% by weight of a decane-soluble component, having a MFR of 1.97 g/10 min, a density of 0.920 g/cm³, a melt tension of 4.6 g and a bulk specific gravity of 0.36 g/cm³, and showing an endothermic curve (measured by DSC) with the maximum peak at 103° C.

EXAMPLE 8

[Polymerization]

A polymerization procedure similar to that of Example 4 was repeated except that there were used 50 Nml of hydrogen and a prepolymerized catalyst in an amount of 0.75 mmole in terms of triisobutylaluminum, and that polymerization was carried out at 85° C. and the total pressure of 7 kg/cm²-G, whereby there was obtained 141 g of an ethylene/1-butene copolymer containing 6.8% by weight of 1-butene constituent units and 0.67% by weight of a decane-soluble component, having a MFR of 1.99 g/10 min, a density of 0.920 g/cm³, a melt tension of 6.0 g and a bulk specific gravity of 0.37 g/cm³.

EXAMPLE 9

[Preparation of a prepolymerized catalyst]

To 1.11 g of the same silica as used in Example 1 was added 15 ml of toluene to form a suspension. To the suspension was added 7.76 ml of a toluene solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes. Then, to the suspension was added 13.6 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.95 mole/liter) synthesized by a procedure similar to that in Example 1, and the resultant mixture was stirred at room temperature for 35 minutes. Thereafter, to the suspension was added 162.0 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00228 mole/liter), and the resultant mixture was stirred for 30 minutes. To the mixture was added 100 ml of decane, and prepolymerization was carried out at 30° C. for 5 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 20.6 mg of zirconium, 310 mg of aluminum and 27 g of polyethylene based on 1 g of silica.

[Polymerization]

A glass autoclave having a content volume of 1.5 liters and thoroughly purged with nitrogen was charged with 1 Liter of decane, and an ethylene and hydrogen gas mixture was introduced at a flow rate of 250 liter/hr and 1 liter/hr, respectively. The system temperature was raised to 75° C., and to the autoclave was added a mixture of 0.5 mmole of triisobutylaluminum and the above-described prepolymerized catalyst in an amount of 0.005 mg atom in terms of zirconium. Thereafter, polymerization was carried out at 75° C. and a normal pressure for 3 hours while the above-mentioned gas mixture was being fed continuously, whereby polymerization progressed in a slurry state.

After the completion of the polymerization, the resultant polymer was recovered by filtering, and dried overnight at 80° C. under reduced pressure to obtain 16.9 g of an ethylene polymer having a MFR of 1.18 g/10 min and a melt tension of 6.5 g.

EXAMPLE 10

[Preparation of a catalyst]

A 100 ml egg-plant type flask thoroughly purged with nitrogen was charged with 20 ml of decane, 27.9 ml of a toluene solution of an organoaluminum oxy-compound (Al: 0.716 mole/liter) and 37.3 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00268 mole/liter), and the contents were stirred for 5 minutes. Toluene was distilled off from the mixture over a period of 2 hours using an evaporator at room temperature under reduced pressure. The resultant precipitated solid product was recovered by filtering, washed with hexane, and dried at room temperature under reduced pressure to obtain a solid catalyst having an Al/Zr atomic ratio of 112.

[Polymerization]

A polymerization procedure similar to that in Example 1 was repeated except that only the solid catalyst component prepared above was used as a catalyst component in an amount of 0.005 mg atom in terms of zirconium, and that ethylene homopolymerization was carried out at 85° C. for 1 hour at the total pressure of 8 kg/cm²-G, whereby 26.4 g of an ethylene homopolymer having a MFR of 0.42 g/10 min and a melt tension of 12.0 g was obtained.

EXAMPLE 11

[Polymerization]

A polymerization procedure similar to that in Example 10 was repeated except that 100 Nml of hydrogen was added, whereby 34.0 g of an ethylene homopolymer having a MFR of 3.10 g/10 min and a melt tension of 5.0 g was obtained.

Comparative Example 2

[Polymerization]

A polymerization procedure similar to that in Example 9 was repeated except that there were used toluene as a solvent, and an ethylene, 1-butene (both being polymerization monomers) and hydrogen gas mixture at a flow rate of 285 liter/hr, 15 liter/hr and 2 liter/hr, respectively and that copolymerization was carried out for 20 minutes, whereby polymerization progressed in a solution state. After the completion of the polymerization, the resultant polymer was recovered by precipitating it in a large amount of methanol, and dried overnight at 130° C. under reduced pressure, whereby there was obtained 33.1 g of an ethylene/1-butene copolymer containing 6.5% by weight of 1-butene constituent units, having a MFR of 1.44 g/10 min, a density of 0.922 g/cm³ and a melt tension of 2.1 g.

Comparative Example 3

[Polymerization]

A polymerization procedure similar to that in Example 9 was repeated except that the flow rates of ethylene and hydrogen in the gas mixture were altered to 100 liter/hr and 5 liter/hr, respectively, that there were used as catalyst components 3.42 ml of a toluene solution of the organoaluminum oxy-compound (Al: 1.46 mole/liter) and 0.33 ml of a toluene solution of ethylenebis(indenyl)-zirconium dichloride (Zr: 0.00150 mole/liter), and that ethylene homopolymerization reaction was carried for 80 minutes, whereby the polymerization progressed in a cloudy state. After the completion of the polymerization, the resultant polymer was recovered by precipitating it in a large amount of methanol, and dried overnight at 80° C. under reduced pressure, whereby there was obtained 8.2 g of an ethylene copolymer having a MFR of 0.72 g/10 min and a melt tension of 2.9g.

Example 12

[Preparation of a prepolymerized catalyst]

An 8 liter flask thoroughly purged with nitrogen was charged with 55.4 g of silica (TG-20643, manufactured by Fuji Davison K.K.) which was fired at 700° C. for 6 hours before charging and 1 liter of decane to form a suspension. To the suspension was added 46 mmoles of triisobutylaluminum diluted with 50 ml of decane, and the mixture was stirred at room temperature for 10 minutes.

Successively, 140 ml of a toluene solution of the catalyst component (ii) (manufactured by Schering Co., Ltd.) prepared above (Al: 1.65 mole/liter) was added, and the mixture was stirred at room temperature for 10 minutes. Then, 36.9 ml of a toluene solution of bis (methylcyclopentadienyl) zirconium dichloride (Zr: 0.05 mole/liter) was added, and the mixture was stirred for 15 minutes. Then, prepolymerization was carried out at 30° C. for 3.5 hours by continuously introducing ethylene at a normal pressure.

Thereafter, there were successively added 2 liters of decane, 279 ml of the catalyst component (ii), 2.79 liters of the catalyst component (i) (Zr: 0.00264 mole/liter) prepared in Example 1, and 23.4 ml of triisobutylaluminum diluted with 50 ml of decane, and prepolymerization was carried out at 30° C. for 4 hours.

After the completion of the prepolymerization, the solvent was removed by decantation, washed at 60° C. 3 times with 5 liters of hexane, and further washed 3 times at room temperature with 5 liters of hexane, whereby there was obtained a prepolymerized catalyst containing 11 mg of Zr, 190 mg of Al and 16 g of polyethylene based on 1 g of silica.

[Polymerization]

Copolymerization of ethylene with 1-hexene was carried out using a continuous fluidized bed gas phase polymerization equipment at a polymerization temperature of 80° C. and the total pressure of 20 kg/cm^2-G by continuously feeding the above-described prepolymerization catalyst at a rate of 0.1 mmole/hr in terms of zirconium and 15 mmole/hr in terms of triisobutylaluminum, and also continuously supplying ethylene, 1-hexene, hydrogen and nitrogen to maintain the following constant gas composition during polymerization: a 1-hexene/ethylene volume ratio of 0.015 and a H_2/ethylene volume ratio of 6.3×10^{-3}. The polymer yield was 6.0 kg/hr.

The thus obtained polymer contained 10.7% by weight of 1-hexene constituent units and 0.53% by weight of a decane-soluble component measured at 23° C., had a MFR of 1.60 g/10 min, a density of 0.922 g/cm^3 a melt tension (MT) of 6.6 g and a bulk specific gravity of 0.38 g/cm^3 and showed an endothermic curve (measured by DSC) with the maximum peak at 112.1° C.

The results are shown in Tables 1 and 2.

TABLE 1

	Polymerization Conditions								
Example	Catalyst component (mg atom-Zr)		(i-Bu)$_3$Al (mmole)	Total pressure (kg/cm^2-G)	1-Butene (mol %)	H_2 (Nml)	Temp. (°C.)	Time (h)	Note
1	(Ex. 1)	0.0075	1.13	4	6.3	50	80	1	
2	(Ex. 2)	0.0050	0.75	4	3.6	10	70	2	
3	(Ex. 3)	0.0075	1.13	4	6.3	30	80	1	
4	(Ex. 4)	0.0050	0.50	4	4.4	30	80	1	
5	(Ex. 1)	0.0050	0.75	4	3.6	30	70	1	
6	(Ex. 1)	0.0030	0.54	8	—	50	85	1	
7	(Ex. 3)	0.0050	0.50	2.5	3.9	50	80	1	
8	(Ex. 4)	0.0050	0.75	7	4.4	50	85	1	
9	(Ex. 9)	0.0050	0.50	normal pressure	—	(1 l/h)	75	3	Ethylene 250 l/h
10	(Ex. 10)	0.0050	—	8	—	50	85	1	
11	(Ex. 10)	0.0050	—	8	—	100	85	1	
12	(Ex. 12) (0.1 mmole/h)		(15 mmole/h)	20	—	—	80	—	
Comp. Ex. 1	(Comp. Ex. 1)	0.0150	0.75	8	6.1	50	85	1	
Comp. Ex. 2	(Ex. 9)	0.0050	0.50	normal pressure	(15 l/h)	(2 l/h)	75	0.33	Ethylene 285 l/h
Comp. Ex. 3	(Comp. Ex. 3)	0.0005	5.00	normal pressure	—	(5 l/h)	75	0.33	Ethylene 100 l/h

TABLE 2

Example	Yield (g)	1-Butene content (wt. %)	Polymerization results MFR (g/10 min.)	Density (g/cm³)	Decane-sol. component (wt. %)	Melt tension (g)	DSC max. peak temp. (°C.)	Bulk sp. gr. (g/cm³)
1	116	8.1	2.30	0.915	2.8	3.3	94	0.31
2	88	6.7	0.48	0.922	0.25	11	103	0.35
3	149	10.1	1.78	0.912	3.1	5.3	94	0.36
4	48	6.5	3.10	0.922	0.32	4.9	115	0.24
5	95	7.4	0.075	0.920	0.18	42	103	0.32
6	121	—	0.29	—	—	17.5	—	0.36
7	119	7.0	1.97	0.920	0.35	4.6	103	0.37
8	141	6.8	1.99	0.920	0.67	6.0	—	—
9	16.9	—	1.18	—	—	6.5	—	—
10	26.4	—	0.42	—	—	12.0	—	—
11	34.0	—	3.10	—	—	5.0	—	—
12	(6.0 kg/h)	10.7 (1-hexene content)	1.60	0.922	0.53	6.6	112.1	0.38
Comp. Ex. 1	137	7.2	1.29	0.920	1.1	1.9	114	—
Comp. Ex. 2	33.1	6.5	1.44	0.922	—	2.1	—	—
Comp. Ex. 3	8.2	—	0.72	—	—	2.9	—	—

Comparative Example 4

[Preparation of a prepolymerized catalyst]

Comparative Example 1 was repeated except that 13.1 ml of a toluene solution of bis(cyclopentadienyl)-zirconium dichloride (Zr: 0.04 mole/liter) was used in place of the toluene solution of bis(methylcyclopentadienyl)-zirconium dichloride to obtain a prepolymerized catalyst containing 8.7 mg of zirconium, 290 mg of aluminum and 7.7 g of polyethylene based on 1 g of silica.

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there were used a gas mixture containing 6.7 mol % of 1-butene and the prepolymerized catalyst obtained above in an amount of 0.01 mg atom in terms of zirconium and 0.25 mmole in terms of triisobutylaluminum, and that polymerization was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm²-G, whereby there was obtained 75 g of an ethylene/1-butene copolymer containing 6.9% by weight of 1-butene constituent units and 1.5% by weight of a decane-soluble component, having a MFR oil 2.63 g/10 min, a density of 0.922 g/cm³ and a melt tension of 1.3 g, and showing an endothermic curve (measured by DSC) with the maximum peak at 114° C.

Comparative Example 5

[Preparation of a prepolymerized catalyst]

To 1.05 g of the same silica as used in Example 1 was added 20 ml of decane to form a suspension in a 400 ml glass flask. To the suspension was added 2.62 ml of a decane solution of triisobutylaluminum (Al: 1 mole/-liter), and the resultant mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 4.87 ml of a toluene solution of an organoaluminum oxy-compound [prepared by removing toluene from a toluene solution of a methylaluminoxane manufactured by Schering Co., Ltd. and redissolving the residue in toluene (Al: 1.79 mole/liter)], and the resultant mixture was stirred at room temperature for 35 minutes.

Thereafter, to the suspension was added 16.2 ml of a toluene solution of bis(n-butylcyclopentadienyl)zirconium dichloride (Zr: 0.0108 mole/liter), and the mixture was stirred for 30 minutes. Then, 75 ml of decane was further added to the mixture, and prepolymerization was carried out at 30° C. for 4 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that of Example 1 was conducted to obtain a prepolymerized catalyst containing 9.3 mg of zirconium, 150 mg of aluminum and 18 g of polyethylene.

[Polymerization]

A polymerization procedure similar to that of Example 1 was repeated except that there were used a gas mixture containing 6.9 mol % of 1-butene and the prepolymerized catalyst obtained above in an amount of 0.005 mg atom in terms of zirconium and 0.5 mmole in terms of triisobutylaluminum, and that polymerization was carried out for 1 hour at 85° C. and the total pressure of 8 kg/cm²-G, whereby there was obtained 147 g of an ethylene/1-butene copolymer containing 9.6% by weight of 1-butene constituent units and 1.5% by weight of a decane-soluble component, having a MFR of 2.45 g/10 min, a density of 0.910 g/cm³ and a melt tension of 0.95 g, and showing an endothermic curve (measured by DSC) with the maximum peak at 109° C.

Comparative Example 6

A glass autoclave having a content volume of 1.5 liter and thoroughly purged with nitrogen was charged with 1 liter of toluene, and ethylene, 1-butene and hydrogen in a mixture were introduced thereinto at a flow rate of 285 liter/hour, 15 liter/hour and 2 liter/hour, respectively. The system temperature was raised to 70° C. and polymerization was started after introducing 0.5 mmole of triisobutylaluminum and the prepolymerized catalyst prepared in Example 1 in an amount of 0.005 mg atom in terms of zirconium.

Polymerization was carried out for 20 minutes at 75° C. and a normal pressure by continuously introducing the above-mentioned gas mixture, whereby the polymerization progressed while dissolving the produced polymer in toluene. After the completion of polymerization, the resultant polymer was precipitated by pouring the polymer solution in methanol.

Then, the precipitated polymer was recovered by filtering, and dried overnight at 80° C. under reduced pressure, whereby there was obtained 33.1 g of an ethylene/1-butene copolymer having a MFR of 1.44 g/10 min, a density of 0.922 g/cm³ and a melt tension (MT) of 2.1 g.

Comparative Example 7

A glass autoclave having a content volume of 1.5 liter and thoroughly purged with nitrogen was charged with 1 liter of toluene, and ethylene, 1-butene and hydrogen in a mixture were introduced at a flow rate of 285 liter/hour, 15 liter/hour and 5 liter/hour, respectively. The system temperature was raised to 70° C. and polymerization was initiated by introducing the organoaluminum oxy-compound prepared in Example 1 in an amount of 5.0 mg atom in terms of aluminum and the catalyst component (i) in an amount of 0.0005 mg atom in terms of zirconium.

The polymerization was carried out for 20 minutes at 75° C. and a normal pressure while the above-described gas mixture was being continuously introduced, whereby the polymerization progressed while dissolving the produced polymer in toluene. A subsequent operation similar to that in Comparative Example 4 was repeated to obtain 44.1 g of an ethylene/1-butene copolymer having a MFR of 1.08 g/10 min, a density of 0.928 g/cm^3 and a melt tension (MT) of 2.0 g.

EXAMPLE 13

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

A 400 ml glass flask thoroughly purged with nitrogen was charged with 1.38 g of silica (F-498, manufactured by Fuji Davison K.K.) which was fired at 700° C. for 6 hours before charging and 20 ml of decane to form a suspension. To the suspension was added 3.24 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the contents were stirred at room temperature for 30 minutes.

To the suspension was added 18.8 ml of a toluene solution of an organoaluminum oxy-compound (prepared by drying methylaluminoxane manufactured by Schering Co., Ltd, and redissolving the residue in toluene, Al: 0.864 mole/liter), and the mixture was further stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 1.03 ml of a toluene solution of bis(cyclopentadienyl)zirconium dichloride (Zr: 0.0417 mole/liter), and the mixture was stirred for 10 minutes. Then, 50 ml of decane was further added, and prepolymerization was carried out at 30° C. for 2 hours by continuously introducing ethylene at a normal pressure.

Thereafter, 100.5 ml of of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00172 mole/liter) was added, and the prepolymerization was continued at 30° C. for 4 hours.

After the completion of the prepolymerization, the solvent was removed by decantation, and the residue was washed 3 times at 60° C. with 250 ml of hexane and then 3 times at room temperature with 250 ml of hexane, whereby there was obtained a prepolymerized solid catalyst containing 9.5 mg atom of zirconium, 0.66 g atom of aluminum and 1750 g of polyethylene.

[Polymerization]

A stainless steel autoclave having a content volume of 2 liters and thoroughly purged with nitrogen was charged with 150 g of sodium chloride (special grade, from Wako Junyaku K.K.), and the contents were dried for 1 hour at 90° C. under reduced pressure. Thereafter, the system pressure was returned to a normal pressure by introducing ethylene, and the system temperature was held at 70° C. Thereafter, the autoclave was charged with a premixture of 0.3 mmole of triisobutylaluminum and the above-described solid catalyst in an amount of 0.003 mg atom in terms of zirconium.

Then, 50 Nml of hydrogen was introduced at first, and then ethylene was further introduced into the autoclave at a system temperature of 70° C. so that the total pressure became 8 kg/cm^2-G, and polymerization was initiated.

Thereafter, the polymerization was carried out at 85° C. for 1 hour while the total pressure was being maintained at 8 kg/cm^2-G by introducing only ethylene. After the completion of the polymerization, sodium chloride was removed from the contents by washing with water. The remaining polymer was washed with methanol, and dried overnight at 80° C. under reduced pressure, whereby there was obtained 142 g of a polymer having a bulk specific gravity of 0.43 g/cm^3, a MFR of 0.65 g/10 min measured at 190° C. and a load of 2.16 kg, a melt tension (MT) of 10 g and an average particle size of 410 μm.

EXAMPLE 14

To 1.12 g of the same silica as used in Example 13 was added 20 ml of decane to form a suspension. To the suspension was added 2.8 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 35 minutes.

Then, to the suspension was added 10.8 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 0.864 mole/liter), and the mixture was further stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 1.34 ml of a toluene solution of bis(cyclopentadienyl)zirconium dichloride (Zr: 0.0417 mole/liter), and the contents were stirred for 30 minutes. Furthermore, 50 ml of decane was added, and prepolymerization was carried out at 30° C. for 2 hours by continuously introducing ethylene at normal pressure. Thereafter, to the reaction mixture was added 71.3 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00183 mole/liter), and the prepolymerization was continued at 30° C. for 3.5 hours. A subsequent operation similar to that in Example 13 was conducted to obtain a solid catalyst containing 9.6 mg atom of zirconlure, 0.66 g atom of aluminum and 2100 g of polyethylene based on 100 g of silica.

[Polymerization]

The procedure of Example 13 was repeated to obtain 88 g of a polymer having a bulk specific gravity of 0.42 g/cm^3, a MFR of 0.60 g/10 min and an average particle size of 380 μm.

EXAMPLE 15

[Preparation of a solid catalyst (zirconium catalyst)]

To 3.0 g of the same silica as used in Example 13 was added 30 ml of decane to form a suspension. To the suspension was added 7.45 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 17.6 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 2.13 mole/liter), and the contents were stirred at room temperature for 25 minutes.

Thereafter, to the suspension was added 2.14 ml of a toluene solution of bis (methylcyclopentadienyl) zirconium dichloride (Zr: 0.0465 mole/liter), and the contents were stirred for 5 minutes. To the mixture was

further added 100 ml of decane, and prepolymerization was carried out at 25° C. for 2.5 hours by continuously introducing ethylene at a normal pressure continuously. Then, there was added 166.4 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.0024 mole/liter), and the prepolymerization was further continued at 30° C. for 5 hours. A subsequent operation similar to that in Example 13 was conducted, and there was obtained a prepolymerized solid catalyst containing 9.0 mg atom of zirconium, 0.55 g atom of aluminum and 2000 g of polyethylene based on 100 g of silica.

[Polymerization]

The polymerization procedure in Example 13 was repeated except that 0.54 mmole of triisobutylaluminum was used, and that the catalyst component was injected with ethylene into the autoclave having an internal pressure of 6.5 kg/cm^2, whereby there was obtained 124 g of a polymer having a bulk specific gravity of 0 41 g/cm^3 a MFR of 0 58 g/10 min, a melt tension (MT) of 13 g and an average polymer particle size of 400 μm.

Comparative Example 8

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

To 3.05 g of the same silica as used in Example 13 was added 20 ml of decane to form a suspension. To the suspension was added 7.61 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 11.9 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 2.13 mole/liter), and the contents were stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 10.9 ml of a toluene solution of bis(methylcyclopentadienyl)zirconium dichloride (Zr: 0.0465 mole/liter), and the mixture was stirred for 30 minutes. Then, 100 ml of decane was further added, and prepolymerization was carried out at 30° C. for 3.5 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that in Example 13 was repeated, whereby there was obtained a solid catalyst containing 12.0 mg atom of zirconium, 0.71 g atom of aluminum and 790 g of polyethylene based on 100 g of silica. ps [Polymerization]

The polymerization procedure in Example 15 was repeated except that the prepolymerized solid catalyst obtained above was used in an amount of 0.015 mg atom in terms of zirconium to obtain 70 g of a polymer having a specific bulk gravity of 0.42 g/cm^3 and a MFR of 0.69 g/10 min.

Comparative Example 9

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

To 1.16 g of the same silica as used in Example 13 was added 20 ml of decane to form a suspension. To the suspension was added 4.05 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 30 minutes.

Then, to the suspension was added 3.17 ml of a toluene solution of the same organoaluminum oxy-compound as in Example 13 (Al: 2.13 mole/liter), and the contents were stirred at room temperature for 30 minutes.

Thereafter, to the suspension was added 80.5 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.0024 mole/liter), and the mixture was stirred for 30 minutes. Then, 50 ml of decane and 90 ml of toluene were further added, and prepolymerization was carried out at 30° C. for 3 hours by continuously introducing ethylene at a normal pressure. A subsequent operation similar to that in Example 13 was repeated, whereby there was obtained a prepolymerized solid catalyst containing 8.9 mg atom of zirconium, 0.56 g atom of aluminum and 1000 g of polyethylene based on 100 g of silica.

[Polymerization]

The polymerization procedure in Example 15 was repeated to obtain 123 g of a polymer having a specific bulk gravity of 0.36 g/cm^3, a MFR of 0.44 g/10 min and a polymer average particle size of 370 μm.

EXAMPLE 16

[Polymerization]

The polymerization procedure in Example 13 was repeated except that there were used a gas mixture of ethylene and 1butene (1-butene content: 3.9 mol %) in place of ethylene, 30 Nml of hydrogen, 0.75 mmole of triisobutylaluminum and the solid catalyst component prepared in Example 3 in an amount of 0.0075 mg atom in terms of zirconium, and that the polymerization temperature and total pressure were set at 80° C. and 2.5 kg/cm^2-G, respectively, whereby there was obtained 172 g of a polymer having a bulk specific gravity of 0.38 g/cm^3, a MFR of 0.82 g/10 min, a melt tension (MT) of 9 g and a density of 0.913 g/cm^3.

EXAMPLE 17

[Preparation of a prepolymerized solid catalyst (zirconium catalyst)]

To 1.49 g of the same silica as in Example 13 was added 25 ml of decane to form a suspension. To the suspension was added 3.72 ml of a decane solution of triisobutylaluminum (Al: 1 mole/liter), and the mixture was stirred at room temperature for 45 minutes.

Then, to the suspension was added 8.09 ml of the same organoaluminum oxy-compound as in Example 13 (Al: 2.30 mole/liter), and the contents were further stirred at room temperature for 45 minutes.

Thereafter, to the suspension was added 2.13 ml of a toluene solution of bis(methylcyclopentadienyl)zirconium dichloride (Zr: 0.0465 mole/liter), and the contents were stirred for 10 minutes. To the mixture was further added 75 ml of decane, and prepolymerization was carried out at 30° C. for 1.5 hours by continuously introducing ethylene at a normal pressure. Thereafter, to the reaction mixture was added 51.9 ml of a toluene solution of ethylenebis(indenyl)zirconium dichloride (Zr: 0.00287 mole/liter), and the prepolymerization was continued at 30° C. for 4 hours, whereby there was obtained a prepolymerized solid catalyst containing 11.5 mg atom of zirconium, 0.71 g atom of aluminum and 1700 g of polyethylene based on 100 g of silica.

[Polymerization]

The polymerization procedure in Example 13 was repeated except that there were used a gas mixture of ethylene and 1-butene (1-butene content: 4.4 mol %) in place of ethylene, 30 Nml of hydrogen, 0.5 mmole of triisobutylaluminum and the prepolymerized solid catalyst component prepared above in an amount of 0.005 mg atom in terms of zirconium, whereby there was obtained 137 g of a polymer having a bulk specific gravity of 0.39 g/cm^3, a MFR of 0.53 g/10 min, a melt tension (MT) of 12 g and a density of 0.917 g/cm^3.

What is claimed is:

1. An ethylene copolymer comprising constituent units (a) derived from ethylene and constituent units (b) derived from an α-olefin having 3 to 20 carbon atoms, which is characterized in that:

(A) the ethylene copolymer has a density (d) of 0.87 to 0.94 g/cm^3;

(B) the ethylene copolymer has a MFR of 0.001 to 50 g/10 min as measured at a temperature of 190° C. and a load of 2.16 kg;

(C) the melt tension (MT) and MFR of the ethylene copolymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6; \text{ and}$$

(D) the temperature (T) at which the endothermic curve of the ethylene copolymer measured by a differential scanning calorimeter (DSC) shows the highest peak and the density (d) satisfy the relation

$$T < 400(d) - 250.$$

2. The ethylene copolymer as claimed in claim 1, wherein the ethylene copolymer comprises the constituent units derived from ethylene in an amount of 70 to 96% by weight, and the constituent units derived from an α-olefin in an amount of 4 to 30% by weight.

* * * * *

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(19)(CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Olefin Copolymers and Processes for Preparing Same

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(JP) 189044/1989 1989/07/21

(57) 9 Claims

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ABSTRACT

In accordance with the present invention, there are provided ethylene copolymers composed of structural units (a) derived from ethylene and structural units (b) derived from α-olefin of 3 - 20 carbon atoms, said ethylene copolymers having

[A] a density of 0.85 - 0.92 g/cm^3,

[B] an intrinsic viscosity [η] as measured in decalin at 135°C of 0.1 - 10 dl/g,

[C] a ratio ($\overline{M}w/\overline{M}n$) of a weight average molecular weight ($\overline{M}w$) to a number average molecular weight ($\overline{M}n$) as measured by GPC of 1.2 - 4, and

[D] a ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg at 190°C of 8 - 50, and being narrow in molecular weight distribution and excellent in flowability.

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TITLE

OLEFIN COPOLYMERS AND PROCESSES FOR PREPARING SAME

FIELD OF THE INVENTION

This invention relates to novel ethylene copolymers and process for preparing the same and more particularly to novel ethylene copolymers excellent in flowability in spite of the fact that they are narrow in molecular weight distribution ($\bar{M}w/\bar{M}n$) in comparison with conventionally known ethylene copolymers, and to process for preparing the same.

In a further aspect, the invention relates to novel propylene random copolymers and process for preparing the same and more particularly to novel propylene random copolymers having low melting points in comparison with conventionally known propylene random copolymers and, in particular, excellent in heat-sealing properties and anti-block properties, and to process for preparing the same.

In another aspect, the invention, relates to olefin polymerization catalysts capable of polymerizing olefins with excellent polymerization activity even when the amount of aluminoxane used is reduced and capable of giving olefin polymers having high molecular weights.

BACKGROUND OF THE INVENTION

When molded into articles such as film, copolymers of ethylene and α-olefins of 3 to 20 carbon atoms are found to have excellent mechanical strength such as tensile strength, tear strength or impact strength and also excellent heat resistance, stress crack resistance, optical characteristics and heat-sealing properties in comparison with conventional high-pressure low density polyethylenes, and are known as materials particularly useful for the preparation of inflation film or the like.

Generally speaking, the ethylene copolymers mentioned above have such excellent characteristics that when said copolymers come to be narrower in molecular weight distribution represented by the ratio ($\overline{M}w/\overline{M}n$) of weight average molecular weight ($\overline{M}w$) to number average molecular weight ($\overline{M}n$), the molded articles obtained therefrom, such as film, are found to be less tacky. However, when these ethylene copolymers having a narrow molecular weight distribution are melted, there was such drawbacks that their flowability represented by the ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg as measured at 190°C is small, with the result that they become poor in moldability.

Therefore, if ethylene copolymers which are small in value of $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, large in value of MFR_{10}/MFR_2 and excellent in

flowability come to be obtained, such ethylene copolymers are certainly of great commercial value.

On the other hand, polypropylene has wide applications in the field of plastics because of its excellent physical properties. For example, polypropylene is widely used as packaging film material. In the applications of the type, however, because of its relatively high melting point, polypropylene is generally copolymerized with ethylene or α-olefins of 4 to 20 carbon atoms in order to improve heat-sealing properties at low temperature, and is used in the form of propylene/α-olefin copolymer.

Packaging films formed from these known propylene/α-olefin copolymers are still not sufficient in heat-sealing properties, though they are excellent in transparency and scratch resistance in comparison with those formed from low density polyethylene, and accordingly it is hoped that propylene/α-olefin copolymers excellent in heat-sealing properties even at lower temperatures will come to be obtained.

It is well known that the above-mentioned propylene/α-olefin random copolymers may be improved in heat-sealing properties by increasing the proportion of ethylene or α-olefin of 4 to 20 carbon atoms to propylene in the copolymer. However, if the proportion of ethylene or α-olefin of 4 to 20 carbon atoms is increased in the copolymerization, the

resulting propylene/α-olefin copolymer increases in amount of the solvent-soluble component, whereby the resultant copolymer come to be poor in anti-blocking properties and also in stiffness.

Such propylene/α-olefin random copolymers excellent in heat-sealing properties, anti-block properties and stiffness as mentioned above are available only when they have a low melting point in spite of the fact that the proportion of α-olefin in the copolymer is small.

Incidentally, olefin polymerization catalysts composed generally of titanium compounds or vanadium compounds and organoaluminum compounds have heretofore been used for preparing ethylene copolymers. In recent years, however, catalysts composed of zirconium compounds and aluminoxane have been proposed of late as new Ziegler polymerization catalysts. Japanese Patent L-O-P Publn. No. 19309/1983 discloses a process for polymerizing ethylene and one or two or more C_3-C_{12} α-olefins at a temperature of from -50°C to 200°C in the presence of a catalyst composed of a transition metal containing compound represented by the following formula

(Cyclopentadienyl)$_2$MeHal

wherein R is cyclopentadienyl, C_1-C_6 alkyl or halogen, Me is a transition metal, and Hal is halogen, and a linear aluminoxane represented by the following formula

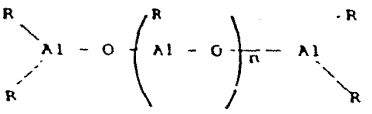
$$Al_2OR_4(Al(R)-O)_n$$

wherein R is methyl or ethyl, and n is a number of 4-20, or a cyclic aluminoxane represented by the following formula

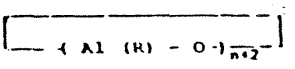
$$[-(Al(R)-O)_{n+2}-]$$

wherein R and n are as defined above. The publication cited above describes that ethylene should be polymerized in the presence of small amounts, up to 10% by weight, of somewhat long chain α-olefins or mixtures thereof in order to control a density of the resulting polyethylene.

Japanese Patent L-O-P Publn. No. 95292/1984 discloses an invention relating to a process for preparing a linear aluminoxane represented by the following formula

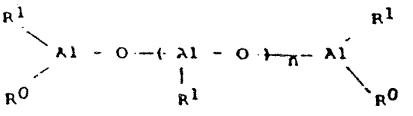


wherein n is 2-40, and R is C_1-C_6 alkyl, and cyclic aluminoxane represented by the following formula,



wherein n and R are as defined above. The publication cited above describes that olefins are polymerized in the presence of the aluminoxane prepared by the process of said publication, for example, methyl aluminoxane in admixture with a bis(cyclopentadienyl) compound of titanium or zirconium, whereupon at least twenty-five million g of polyethylene per g of the transition metal per hour is obtained.

Japanese Patent L-O-P Publn. No. 35005/1985 discloses a process for preparing olefin polymerization catalysts, wherein an aluminoxane compound represented by the following formula



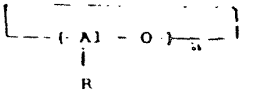
wherein R^1 is C_1-C_{10} alkyl, and R^0 is R^1 or represents -O- by linkage therewith, is first allowed to react with a magnesium compound, the resulting reaction product is then chlorinated,

followed by treating with a Ti, V, Zr or Cr compound. This publication cited above describes that the catalysts prepared by the process of said publication are particularly useful for the copolymerization of mixtures of ethylene and C_3-C_{12} α-olefins.

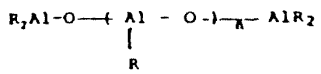
Japanese Patent L-O-P Publn. No. 35006/1985 discloses a combination of (a) mono-, di- or tri-cyclopentadienyl of two or more different transition metals or derivatives thereof and (b) aluminoxane as a catalyst system for preparing reactor blend polymers. Example 1 of the above-cited publication discloses that polyethylene having a number average molecular weight of 15,300, a weight average molecular weight of 36,400 and containing 3.4% of the propylene component has been obtained by polymerization of ethylene with propylene in the presence of a combination of bis(pentamethylcyclopentadienyl)zirconium dimethyl and aluminoxane as the catalyst. Example 2 of the said publication discloses polymerization of ethylene with propylene in the presence of a combination of bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride and aluminoxane as the catalyst, whereby a blend of polyethylene and ethylene/propylene copolymer is obtained, said polyethylene having a number average molecular weight of 2,000, a weight average molecular weight of 8,300 and the

propylene content of 7.1 mol%, and comprising a toluene-soluble portion having a number average molecular weight of 2,200, a weight average molecular weight of 11,900 and the propylene content of 30 mol% and a toluene-insoluble portion having a number average molecular weight of 3,000, a weight average molecular weight of 7,400 and the propylene content of 4.8 mol%. Similarly, Example 3 of the said publication discloses a blend of LLDP and an ethylene/propylene copolymer, said LLDPE comprising a soluble portion having a molecular weight distribution ($\bar{M}w/\bar{M}n$) of 4.57 and the propylene content of 20.6% and an insoluble portion having the molecular weight distribution of 3.04 and the propylene content of 2.5 mol%.

Japanese Patent L-O-P Publn. No. 35007/1985 discloses a process for polymerizing ethylene alone or together with α-olefins of at least 3 carbon atoms in the presence of a catalyst system containing metallocene and a cyclic aluminoxane represented by the following formula



wherein R is alkyl of 1-5 carbon atoms, and n is an integer of 1 to about 20, or a linear aluminoxane represented by the following formula



wherein R and n are as defined above. According to the said publication, the polymers obtained by the above-mentioned process are alleged to have a weight average molecular weight of from about 500 to about 1,400,000 and a molecular weight distribution of 1.5-4.0.

Japanese Patent L-O-P Publn. No. 35008/1985 discloses polyethylene or copolymers of ethylene and C_3-C_{10} α-olefins, both having a broad molecular weight distribution, obtained by using a catalyst system containing at least two kinds of metallocenes and aluminoxane. The said copolymers disclosed in the above-mentioned publication are alleged to have a molecular weight distribution ($\overline{M}w/\overline{M}n$) of 2-50.

Japanese Patent L-O-P Publn. No. 130314/1986 discloses polypropylene high in isotacticity obtained by polymerization of propylene in the presence of a catalyst system comprising a sterically fixed zirconium-chelate compound and aluminoxane.

J. Am. Chem. Soc., 109, 6544 (1987) discloses formation of a high molecular weight isotactic polypropylene obtained by polymerization of propylene in the presence of a catalyst system comprising ethylenebis(indenyl)hafnium dichloride or its hydride and aluminoxane, said isotactic polypropylene

having a narrow molecular weight distribution ($\overline{M}w/\overline{M}n$) of 2.1-2.4.

Japanese Patent L-O-P Publn. No. 142005/1987 discloses a stereoblock polypropylene having $\overline{M}w/\overline{M}n$ of 5.0-14.9 obtained by polymerization of propylene in the presence of a catalyst system comprising tetramethylethylene-bis(cyclopentadienyl) titanium chloride and aluminoxane. The polypropylene thus obtained is short in isotactic chain length and is a rubbery polymer.

The present inventors have come to accomplish the present invention on the basis of their finding that ethylene copolymers which are small in $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, large in MFR_{10}/MFR_2 and excellent in flowability are obtained by copolymerization of ethylene with α-olefins of 3-20 carbon atoms in the presence of olefin polymerization catalysts composed of specific hafnium compounds and organoaluminum oxy-compounds.

Furthermore, the present inventors have found that when propylene and α-olefins of 4-20 carbon atoms are copolymerized in the presence of olefin polymerization catalysts composed of specific hafnium compounds and aluminoxane, there are obtained propylene/α-olefin copolymers which are narrow in molecular weight distribution and small in amount of the α-olefin copolymerized therewith, but are low in melting point in comparison with conventionally known

propylene/α-olefin copolymers, on which the present invention has been based.

Accordingly, the present invention is to solve such problems associated with the prior art as mentioned above, and an object of the invention is to provide ethylene copolymers which are small in $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, which are large in MFR_{10}/MFR_2 and excellent in flowability, and processes for preparing the same.

A further object of the invention is to provide propylene/α-olefin copolymers which are narrow in molecular weight distribution and small in amount of the α-olefin copolymerized therewith but have a low melting point and, moreover, which are excellent in heat-sealing properties and also excellent in anti-block properties and stiffness, and processes for preparing the same.

Another object of the invention is to provide olefin polymerization catalysts, which produce polymers which are narrow in molecular weight distribution in homopolymerization or narrow in molecular weight and composition distribution in copolymerization with high polymerization activities even by the use of small amounts of aluminoxane, furthermore, produce easily polymers which are high in molecular weight.

DISCLOSURE OF THE INVENTION

The ethylene copolymers of the present invention are those having (a) structural units derived from ethylene and (b) structural units derived from α-olefin of 3-20 carbon atoms, which are characterized in that they have

(i) a density of 0.85-0.92 g/cm^3,

(ii) an intrinsic viscosity [η] of 0.1-10 dl/g as measured in decalin at 135°C,

(iii) a ($\overline{M}w/\overline{M}n$) ratio of a weight average molecular weight ($\overline{M}w$) to a number average molecular weight ($\overline{M}n$) of 1.2-4 as measured by GPC, and

(iv) a (MFR_{10}/MFR_2) ratio of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg of 8-50 as measured at 190°C.

The processes for preparing ethylene copolymers of the present invention are characterized in that ethylene and α-olefins of 3-20 carbon atoms are copolymerized so that a density of the resulting copolymers becomes 0.85-0.92 g/cm^3, in the presence of catalysts formed from

(A) hafnium compounds having multidentate coordination compounds as ligands, in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, or hafnium compounds obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel, and

[B] organoaluminum oxy-compounds.

The first propylene/α-olefin random copolymers of the present invention are those having (a) structural units derived from propylene and (b) structural units derived from α-olefins of 4-20 carbon atoms, which are characterized in that they have

(i) 90-99 mol% of said structural units (a) and 1-10 mol% of said structural units (b),

(ii) an intrinsic viscosity [η] of 0.5-6 dl/g as measured in decalin at 135°C,

(iii) a melting point [Tm], as measured by a differential scanning calorimeter, falling within the range of the formula $90<Tm<155-3.5(100-P)$ wherein P is the propylene component (mol%) contained in the copolymer,

(iv) a $(\overline{M}w/\overline{M}n)$ ratio of less than 3.5 between a weight average molecular weight $(\overline{M}w)$ and a number average molecular weight $(\overline{M}n)$ as measured by GPC, and

(v) a boiling trichloroethylene-insoluble matter in an amount of less than 5% by weight.

The processes for preparing the first propylene/α-olefin copolymers of the present invention are characterized in that propylene and α-olefins of 4-20 carbon atoms are copolymerized at a temperature of 40-100°C so that the resulting copolymers have 90-99 mol% of structural units (a) derived from propylene and 1-10 mol% of structural units (b)

derived from the α-olefin, in the presence of catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands, in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

[B] organoaluminum oxy-compounds.

The second propylene/α-olefin random copolymers of the present invention are those having (a) structural units derived from propylene, (b) structural units derived from ethylene and (c) structural units derived from α-olefins of 4-20 carbon atoms, which are characterized in that they have

(i) 90-99 mol% of said structural units (a), 0.5-9.5 mol% of said structural units (b) and 0.5-9.5 mol% of said structural units (c),

(ii) an intrinsic viscosity [η] of 0.5-6 dl/g as measured in decalin at 135°C,

(iii) a melting point [Tm], as measured by a differential scanning calorimeter, falling within the range of the formula $70<Tm<155-5.5(100-P)$ wherein P is the propylene component (mol%) contained in the copolymer, and

(iv) a boiling trichloroethylene-insoluble matter in an amount of less than 5% by weight.

The processes for preparing the second propylene/α-olefin copolymers of the present invention are characterized in that propylene, ethylene and α-olefins of 4-20 carbon atoms are copolymerized so that the resulting copolymers have 90-99 mol% of structural units (a) derived from propylene, 0.5-9.5 mol% of structural units (b) and 0.5-9.5 mol% of structural units (c), in the presence of catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

[B] organoaluminum oxy-compounds.

In accordance with the present invention, there are provided olefin polymerization catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B] organoaluminum oxy-compounds, and

[C] organoaluminum compounds.

In accordance with the present invention, furthermore, there are provided olefin polymerization catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B-1] organoaluminum oxy-compounds formed from tri-n-alkyl aluminum, and

[B-2] organoaluminum oxy-compounds in which at least one hydrocarbon group other than n-alkyl group is bonded to Al atom.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustration of process for the preparation of the olefin copolymers of the present invention.

Fig. 2 is a graph showing the relationship between the propylene content and melting point of the propylene random copolymer of the present invention.

Figs. 3-5 are stepwise illustrative of the method of evaluation of heat-sealing properties of the propylene random copolymer of the present invention.

BEST MODE OF PRACTICING THE INVENTION

The ethylene copolymers of the present invention and processes for preparing the same are illustrated below in detail.

The process for the preparation of the ethylene copolymers of the present invention is illustratively shown in Fig. 1

The ethylene copolymers of the invention are random copolymers of ethylene and α-olefins of 3-20 carbon atoms. The ethylene copolymers have a density of 0.85-0.92 g/cm^3, preferably 0.85-0.91 g/cm^3 and especially 0.85-0.90 g/cm^3.

In this connection, the density of these ethylene copolymers was measured by gradient tube density determination using the strand of ethylene copolymer used at the time of determining MFR$_2$ under a load of 2.16 kg at 190°C.

In these ethylene copolymers, are present desirably structural units (a) derived from ethylene in an amount of 60-96 mol%, preferably 65-95 mol% and especially 70-94 mol%, and structural units (b) derived from α-olefin of 3-20 carbon atoms in an amount of 4-40 mol%, preferably 5-35 mol% and especially 6-30 mol%.

The composition of the copolymer is determined by measuring a spectrum of ^{13}C-NMR of a specimen obtained by dissolving about 200 mg of the copolymer in 1 ml of hexachlorobutadiene in a test tube of 10 mmφ under the conditions of a measurement temperature of 120°C, measurement

frequency of 25.05 MHz, spectrum width of 1500 Hz, pulse repetition time of 4.2 sec. and pulse width of 6 sec.

Alpha olefins of 3-20 carbon atoms used in the present invention include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, etc.

The ethylene copolymers of the present invention desirably have an intrinsic viscosity [η] of 0.1-10 dl/g, preferably 0.5-6 dl/g as measured in decalin at 135°C.

The molecular weight distribution ($\overline{M}w/\overline{M}n$) as obtained by gel permeation chromatography (GPC) of the ethylene copolymers of the invention is 1.2-4, preferably 1.4-3.5 and especially 1.5-3.0. As is evidenced by the foregoing, the ethylene copolymers of the invention are narrow in molecular weight distribution and excellent in anti-block properties.

In this connection, a value of ($\overline{M}w/\overline{M}n$) obtained in the invention was determined by the following procedure in accordance with Takeuchi, "Gel Permeation Chromatography," Maruzen, Tokyo.

(1) Using a standard polystyrene having the known molecular weight (a monodispersed polystyrene produced and sold by Toyo Soda K.K.), molecular weight M and GPC (Gel Permeation Chromatography) count of the sample are measured to prepare a correlation diagram calibration curve of the molecular weight

H and EV (Elution Volume). The concentration of the sample used is maintained at 0.02% by weight.

(2) GPC chromatograph of the sample is taken by GPC measurement, and a number average molecular weight $\overline{M}n$ and a weight average molecular weight $\overline{M}w$, in terms of polystyrene, are calculated from the calibration curve mentioned in the above procedure (1) to obtain a value of $\overline{M}w/\overline{M}n$. In that case, the conditions under which the sample is prepared, and the conditions under which GPC measurement is conducted are as follows:

[Preparation of sample]

(a) The sample is put in an Erlenmeyer flask together with o-dichlorobenzene so that the same amounts to 0.1% by weight.

(b) The Erlenmeyer flask is heated at 140°C and stirred for about 30 minutes to dissolve the sample in o-dichlorobenzene.

(c) The solution is subjected to GPC.

[GPC measurement conditions]

The measurement was conducted under the following conditions.

(a) Apparatus 150C-ALC/GPC manufactured by Waters Co.

(b) Column GMH Type manufactured by Toyo Soda K.K.

(c) Amount of sample 400 µl

(d) Temperature 140°C

(e) Flow rate 1 ml/min

In the ethylene copolymers of the invention, a (MFR_{10}/MFR_2) ratio of MFR_{10} at 190°C under a load of 10 kg to MFR_2 at 190°C under a load of 2.16 kg is 8-50, preferably 8.5-45 and especially 9-40.

Such ethylene copolymers having the MFR_{10}/MFR_2 ratio falling within the range of 8-50 as mentioned above are quite favorable in flowability at the time when they are melted.

In contrast thereto, the aforementioned known ethylene copolymers having the $\overline{M}w/\overline{M}n$ ratio of 1.2-4 will come to have the MFR_{10}/MFR_2 ratio in the range of 4-7, and hence they are poor in flowability at the time when they are melted.

As mentioned above, the ethylene copolymers of the present invention have such excellent characteristics that they have a small molecular weight distribution ($\overline{M}w/\overline{M}n$), and molded articles resulting therefrom are less sticky and, at the same time, they are large in MFR_{10}/MFR_2 and excellent in flowability at the time when they are melted.

The ethylene copolymers of the invention as illustrated above may be prepared by copolymerization of ethylene with α-olefins of 3-20 carbon atoms so that the resulting copolymers have a density of 0.85-0.92 g/cm^3 in the presence of catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups

or substituted groups thereof are linked together via lower alkylene, or hafnium catalyst components obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel, and

[B] organoaluminum oxy-compounds.

The catalyst components [A] used in the invention are hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof, e.g. indenyl group, substituted indenyl group and partially hydrated compounds thereof, are linked together via lower alkylene groups, or compounds obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel.

The above-mentioned hafnium compounds include, for example, the following compounds.

Ethylenebis(indenyl)dimethyl hafnium,

Ethylenebis(indenyl)diethyl hafnium,

Ethylenebis(indenyl)diphenyl hafnium,

Ethylenebis(indenyl)methyl hafnium monochloride,

Ethylenebis(indenyl)ethyl hafnium monochloride,

Ethylenebis(indenyl)methyl hafnium monobromide,

Ethylenebis(indenyl)hafnium dichloride,

Ethylenebis(indenyl)hafnium dibromide,

Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethyl hafnium,

Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methyl hafnium monochloride,

Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride,

Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dibromide,

Ethylenebis(4-methyl-1-indenyl)hafnium dichloride,

Ethylenebis(5-methyl-1-indenyl)hafnium dichloride,

Ethylenebis(6-methyl-1-indenyl)hafnium dichloride,

Ethylenebis(7-methyl-1-indenyl)hafnium dichloride,

Ethylenebis(5-methoxy-1-indenyl)hafnium dichloride,

Ethylenebis(2,3-dimethyl-1-indenyl)hafnium dichloride,

Ethylenebis(4,7-dimethyl-1-indenyl)hafnium dichloride,

Ethylenebis(4,7-dimethoxy-1-indenyl)hafnium dichloride.

The above-mentioned hafnium compounds may contain small amounts of zirconium or titanium. In such a case, the content of zirconium or titanium is less than 1% by weight, preferably less than 0.7% by weight and especially less than 0.5% by weight.

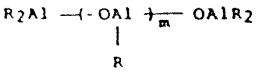
The hafnium catalyst components used in the present invention may include compounds obtained by treating the above-mentioned hafnium compounds with alkylaluminoxylated silica gel. More particularly, the said hafnium catalyst components

may be hafnium compound solutions which are obtained, for example, by passing a solution of the above-mentioned hafnium compound in an organic solvent such as toluene through a column packed with alkylsilylated silica gel, wherein said hafnium compound is brought into contact with the alkylsilylated silica gel.

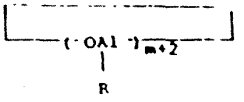
The organic solvents used in that case are preferably aromatic hydrocarbons such as toluene, benzene and xylene. The alkylsilylated silica gel used may includes those obtained by treating silica gel with dimethyl dichlorosilane, ethylmethyl dichlorosilane, trimethyl chlorosilane, trimethyl bromosilane, divinyl dichlorosilane, diethyl dichlorosilane or methylpropyl dichlorosilane. The hafnium concentration in the hafnium compound solution is usually from 1×10^{-5} to 5×10^{-3} mol/l, and the amount of the alkylsilylated silica gel used is usually 20-500 g per 1 mmol of the hafnium compound. A temperature at which the hafnium compound solution is brought into contact with the alkylsilylated silica gel is usually 0-50°C.

When the hafnium catalyst components obtained by treating the above-mentioned hafnium compounds with the alkylsilylated silica gel are used as the catalyst components [A], ethylene copolymers excellent in transparency are obtained.

The catalyst components (B) used in the process of the present invention are organoaluminum oxy-compounds. The organoaluminum oxy-compounds used as the catalyst components may be shown as benzene-soluble aluminoxanes represented by the following general formulas (I) and (II).



(I)



(II)

wherein R may be the same or different and is a hydrocarbon group such as methyl, ethyl, propyl or butyl, preferably methyl or ethyl and especially methyl, and m is an integer of at least 2, preferably at least 5. The above-mentioned aluminoxanes may be prepared, for example, by the procedures as exemplified below.

(1) A procedure which comprises reacting a suspension in a hydrocarbon medium of a compound containing water of absorption or a salt containing water of crystallization, for example, magnesium chloride hydrate, copper sulfate hydrate, aluminumsulfate hydrate, nickel sulfate hydrate or serous chloride hydrate, with trialkylaluminum.

(2) A procedure which comprises reacting trialkylaluminum directly with water, water vapor or ice in a medium such as benzene, toluene, ethyl ether and tetrahydrofuran.

The aluminoxanes as illustrated above may contain small amounts of organometallic components.

Further, the organoaluminum oxy-compounds used in the present invention may be those which are insoluble in benzene. The benzene-insoluble organoaluminum oxy-compounds are illustrated hereinafter.

The benzene-insoluble organoaluminum oxy-compounds used in the invention may be prepared by (i) reaction of organoaluminum compounds with water or (ii) reaction of solutions of aluminoxane, for example, hydrocarbon solutions thereof, with water or active hydrogen-containing compounds.

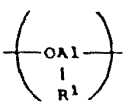
The benzene-insoluble organoaluminum oxy-compounds are considered to have alkyloxyaluminum units represented by the formula $\left(\begin{array}{c} R^1 \\ | \\ -Al-O- \end{array}\right)$ wherein R^1 is hydrocarbon of 1 - 12 carbon atoms and Al component soluble in benzene at 60°C is in an amount, in terms of Al atom, of less than 10%, preferably less than 5% and especially less than 2%, thus they are insoluble or sparingly soluble in benzene.

Solubility in benzene of the organoaluminum oxy-compounds of the present invention is determined by

suspending the organoaluminum oxy-compound equivalent to Al of 100 mg atom in 100 ml of benzene, stirring the suspension at 60°C for 6 hours, filtering the thus treated suspension at a temperature elevated to 60°C using G-5 glass filter equipped with a jacket, washing 4 times the solids portion separated on the filter with 50 ml of benzene kept at 60°C and then measuring the amount of Al atoms (x mmol) present in the total filtrate.

In the alkyloxyaluminum units mentioned above, R^1 is methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, octyl, decyl, cyclohexyl, cyclooctyl, etc. Among these, preferred are methyl and ethyl, particularly methyl.

In addition to the alkyloxyaluminum units of the formula $\left(\begin{array}{c}-\text{O}\underset{\displaystyle R^1}{\underset{|}{\text{Al}}}-\end{array}\right)$, the benzene-insoluble organoaluminum oxy-compounds of the invention may contain oxyaluminum units represented by the formula $\left(\begin{array}{c}-\text{O}\underset{\displaystyle R^2}{\underset{|}{\text{Al}}}-\end{array}\right)$. In the above-mentioned formulas, R^1 is as defined previously, R^2 is hydrocarbon of 1 ~ 12 carbon atoms, alkoxyl of 1 ~ 12 carbon atoms aryloxy of 6 ~ 20 carbon atoms, hydroxyl, halogen or hydrogen, and R^1 and R^2 represent the groups different from each other. In that case, the benzene-insoluble organoaluminum oxy-compounds are preferably those containing the alkyloxyaluminum units

 in the proportion of at least 30 mol%, preferably at least 50 mol% and especially at least 70 mol%.

The organoaluminum compounds (i) used for preparing such benzene-insoluble organoaluminum oxy-compounds as mentioned above are those represented by the formula $R^1_nAlX_{3-n}$ wherein R^1 is hydrocarbon of 1 - 12 carbon atoms, X is halogen, alkoxyl of 1 - 12 carbon atoms, aryloxy of 6 - 20 carbon atoms or hydrogen, and n is 2 - 3.

Such organoaluminum compounds (i) as mentioned above include trialkylaluminum such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum, tridecylaluminum, tricyclohexylaluminum and tricyclooctylaluminum; dialkylaluminum halides such as dimethylaluminum chloride, dimethylaluminum bromide, 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 aryloxides such as diethylaluminum phenoxide. Of these organoaluminum compounds, preferred are those of the above-mentioned general

formula in which R^1 is alkyl and X is chlorine, and particularly preferred is trialkylaluminum.

In this connection, isoprenylaluminum of the general formula $(i\text{-}C_4H_9)_xAl_y(C_5H_{10})_z$ wherein x, y and z are each positive integer, and $z \geq 2x$ may also used as the organoaluminum compound (i).

The organoaluminum compounds (i) as illustrated above may be used either singly or in combination.

The active hydrogen-containing compounds (ii) used in preparing the benzene-insoluble organoaluminum oxy-compounds of the present invention include alcohols such as methyl alcohol and ethyl alcohol, and diols such as ethylene glycol and hydroquinone.

When water is used in preparing the benzene-insoluble organoaluminum oxy-compounds of the present invention, the water may be used after dissolving or suspending in hydrocarbon solvents such as benzene, toluene and hexane, ether solvents such as tetrahydrofuran, and amine solvents such as triethylamine, or may be used in the form of water vapor or ice. As the water, moreover, there may also be used water of crystallization of salt such as magnesium chloride, magnesium sulfate, aluminum sulfate, copper sulfate, nickel sulfate, iron sulfate and cerrous chloride, or water of adsorption adsorbed to inorganic compounds such as silica, alumina and aluminum hydroxide or polymers.

As mentioned above, the benzene-insoluble organoaluminum oxy-compounds of the present invention may be prepared by reaction of the organoaluminum compound (i) with water, or by reaction of a solution of aluminoxane, for example, a hydrocarbon solution thereof, with water or the active hydrogen containing compound. In preparing the benzene-insoluble organoaluminum oxy-compound from the organoaluminum compound and water, the organoaluminum compound is brought into contact with water in a solvent, for example, a hydrocarbon solvent, and in that case, the water is added to the reaction system so that the organoaluminum atoms dissolved in the reaction system become less than 20% based on the total organoaluminum atom. In obtaining the benzene-insoluble organoaluminum oxy-compounds according to the procedure as mentioned above, it is desirable that the water is brought into contact with the organoaluminum compound in the proportion of 1 - 5 moles, preferably 1.5 - 3 moles of the water to 1 mole of the organoaluminum compound.

The above-mentioned reaction for forming the benzene-insoluble organoaluminum oxy-compounds is carried out in solvents, for example, hydrocarbon solvents. The solvents used include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene, aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as

cyclopentane, cyclooctane, cyclodecane and cyclododecane, such hydrocarbon solvents, for example, petroleum fractions, as gasoline, kerosine and gas oil, halides of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, especially chlorides and bromides thereof, and ethers such as ethyl ether and tetrahydrofuran. Among these hydrocarbon media as exemplified above, particularly preferred are aromatic hydrocarbons.

A concentration in terms of Al atom of the organoaluminum compound in the reaction system is desirably 1×10^{-3} to 5 gram atom/l preferably 1×10^{-2} to 3 gram atom/l, and a concentration in the reaction system of water such as water of crystallization is usually 1×10^{-3} to 20 mol/l, preferably 1×10^{-2} to 10 mol/l. In that case, it is desirable that the organoaluminum atoms dissolved in the reaction system are less than 20%, preferably less than 10% and especially in the range of from 0 to 5% based on the total organoaluminum atom.

Contact of the organoaluminum compound with water may be carried out, for example, by the following procedures.

(1) A procedure wherein a hydrocarbon solution of organoaluminum is brought into contact with a hydrocarbon solvent containing water.

(2) A procedure wherein water vapor is blown into a hydrocarbon solution of organoaluminum, thereby bringing the organoaluminum into contact with the water vapor.

(3) A procedure wherein a hydrocarbon solution of organoaluminum is mixed with a hydrocarbon suspension of a compound containing water of adsorption or a compound containing water of crystallization, thereby bringing the organoaluminum into contact with the water of adsorption or water of crystallization.

(4) A procedure wherein a hydrocarbon solution of organoaluminum is brought into contact with ice.

The above-mentioned reaction of the organoaluminum with water is carried out usually at a temperature of from -100 to 150°C, preferably -50 to 100°C and especially -30 to 80°C. The reaction time, though it may largely vary depending upon the reaction temperature, is usually from 1 to 200 hours, preferably 2 to 100 hours.

In preparing the benzene-insoluble organoaluminum oxy-compounds from a solution of aluminoxane and water or a active hydrogen-containing compound, the aluminoxane present in the solution of aluminoxane is brought into contact with water or the active hydrogen-containing compound.

The solution of aluminoxane is a solution of aluminoxane in such a solvent as used in forming the above-mentioned benzene-insoluble organoaluminum oxy-compounds, preferably

aromatic hydrocarbons such as benzene and toluene, and this solution may contain other components so long as they do not affect adversely the reaction between the aluminoxane and water or the active hydrogen-containing compound.

The amount of water or the active hydrogen-containing compound used in the above-mentioned reaction is 0.1 to 5 moles, preferably 0.2 to 3 moles based on 1 gram atom of aluminum present in the solution of aluminoxane. A concentration in the reaction system of aluminoxane in terms of aluminum atom is usually 1×10^{-3} to 5 gram atom/l, preferably 1×10^{-2} to 3 gram atom/l, and a concentration in the reaction system of water is usually 2×10^{-4} to 5 mole/l, preferably 2×10^{-3} to 3 mole/l.

Taking, as an example, the reaction of the solution of aluminoxane with water, said solution of aluminoxane is brought into contact with water or the active hydrogen-containing compound, for example, by the following methods.

(1) A method which comprises bringing the solution of aluminoxane into contact with a hydrocarbon solvent containing water.

(2) A method which comprises blowing water vapor into the solution of aluminoxane, thereby bringing the aluminoxane present in the solution of aluminoxane into contact with the water vapor.

(3) A method which comprises mixing the solution of aluminoxane with a hydrocarbon solution of a compound containing water of adsorption or a compound containing water of crystallization, thereby bringing the aluminoxane present in the solution of aluminoxane into contact with the water of adsorption or water of crystallization.

(4) A method which comprises bringing the solution of aluminoxane into contact directly with water or ice.

The above-mentioned procedures may also be applied to the case wherein the active hydrogen-containing compound (II) is used instead of water.

The reaction of the solution of aluminoxane with water or the active hydrogen-containing compound as illustrated above may be carried out usually at a temperature of from -50° to 150°C, preferably 0° to 120°C and especially 20 - 100°C. The reaction temperature, though it may largely vary depending upon the reaction temperature, is usually 0.5 - 300 hours, preferably about 1 - 150 hours.

In preparing the ethylene copolymers by using the olefin polymerization catalysts as mentioned above, a concentration in the polymerization system of the hafnium compound in terms of hafnium atom is usually 10^{-8} to 10^{-2} gram atom/l, preferably 10^{-7} to 10^{-3} gram atom/l.

The above-mentioned organoaluminum oxy-compounds are desirably used in an amount in terms of aluminum atom in

present in the reaction system of 10^{-4} to 10^{-1} gram atom/l, preferably 5×10^{-4} to 5×10^{-2} gram atom/l.

The polymerization temperature employed is from -50° to 150°C, preferably from 0° to 120°C.

The olefin polymerization mentioned above is carried out usually in vapor phase or liquid phase. In the liquid phase polymerization, the solvent used may be inert hydrocarbon, or the olefin itself may also be used as the solvent.

The hydrocarbon used in that case includes aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane, aromatic hydrocarbons such as benzene, toluene and xylene, and petroleum fractions such as gasoline, kerosine and gas oil.

The polymerization pressure employed is usually from ordinary pressure to 100 kg/cm^2, preferably from ordinary pressure to 50 kg/cm^2, and the polymerization may be carried out batchwise, semi-continuously or continuously. A molecular weight of the resulting polymer may be modified by the addition of hydrogen and/or by regulation of the polymerization temperature employed.

Hereinafter, the first propylene/α-olefin random copolymers and process for preparing the same of the present invention are illustrated in detail.

The propylene/α-olefin random copolymers of the present invention are random copolymers of propylene and α-olefins of 4 - 20 carbon atoms. The propylene/α-olefin random copolymers of the invention desirably contain structural units (a) derived from propylene in an amount of 90 - 99 mol%, preferably 92 - 98 mol%, and structural units (b) derived from α-olefin in an amount of 1 - 10 mol%, preferably 2 - 8 mol%. When the structural units (a) derived from propylene contained in the propylene/α-olefin random copolymer are less than 90 mol%, said copolymer tends to become poor in anti-blocking properties and stiffness and, on the other hand, when said units (a) are in excess of 99 mol%, said copolymer tends to increase in melting point and become poor in heat-sealing properties.

α-olefins of 4 - 20 carbon atoms used herein include 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octane, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Among these, particularly preferred is 1-butene.

The propylene/olefin random copolymers of the present invention desirably have an intrinsic viscosity [η] of 0.5 - 6 dl/g, preferably 1 - 5 dl/g as measured in decalin at 135°C. If this intrinsic viscosity is less than 0.5 dl/g, the copolymers tend to become poor in anti-blocking properties and toughness and, on the other hand if said

intrinsic viscosity exceeds 6 dl/g, the copolymers tend to become port in moldability.

Further, the propylene/α-olefin random copolymers of the invention have a melting point [Tm] as measured by a differential scanning calorimeter falling within the range of

$$90 < Tm < 155 - 3.5\,(100 - P),$$ preferably

$$100 < Tm < 150 - 3.5\,(100 - P)$$

wherein P is the content (mol%) of propylene in the copolymer.

In Fig. 2, there is shown as a straight line A the schematic relationship between the melting point Tm of the above-mentioned propylene/α-olefin random copolymer and the propylene content (mol%) present in said copolymer. In this Fig. 2, there is also shown as a straight line B the relationship between the melting point Tm of the known propylene/α-olefin random copolymer and the propylene content (mol%) present in said copolymer.

As is clear from Fig. 2, the melting point of the first propylene/α-olefin random copolymers of the present invention is lower by 10 ~ 20°C than that of the known propylene/α-olefin random copolymers when the amount of α-olefin copolymerized of the former is the same as that of the latter. Accordingly, films obtained from the first propylene/α-olefin random copolymers of the invention are excellent particularly in heat-sealing properties at low

temperatures, and the films exhibit excellent heat-sealing properties even when they have small amounts of the copolymerized α-olefin, and hence they are excellent in anti-blocking properties and have excellent stiffness.

In the present invention, the propylene/α-olefin random copolymer was allowed to stand in a differential scanning calorimeter (DSC) at 200°C for 5 minutes, cooled up to 20°C at a rate of 10°C/min, and allowed to stand at 20°C for 5 minutes, and then the temperature was elevated from 20°C to 200°C at a rate of 10°C/min to obtain a temperature (Tm) at a maximum endothermic peak which was then taken as a melting point of said propylene/α-olefin random copolymer.

The molecular weight distribution ($\overline{M}w/\overline{M}n$) of the first propylene/α-olefin random copolymers of the invention as obtained by gel permeation chromatography (GPC) is less than 3.5, preferably less than 3.0 and especially less than 2.5. As stated above, the first propylene/α-olefin random copolymers of the invention are narrow in molecular weight distribution and, from this point, they have excellent anti-blocking properties.

The determination of melting point was conducted by using about 2.5 mg of the specimen and DSC of Perkin Elmer-7 Model at heat-up rate of 10°C/min.

The first propylene/α-olefin random copolymers of the invention are desirably to have a soluble portion in boiling

n-pentane in an amount of less than 3% by weight, preferably less than 2% by weight and especially less than 1% by weight.

Further, the first propylene/α-olefin random copolymers of the invention are desirably to have an insoluble portion in boiling trichloroethylene in an amount of less than 5% by weight, preferably less than 3% by weight and especially less than 1% by weight.

The amounts of the insoluble portion in boiling trichloroethylene and the soluble portion in boiling n-pentane were determined by such a manner that about 3 g of the finely pulverized specimen was extracted for 5 hours with 180 ml of each of the solvents in a cylindrical filter paper by using a Soxhlet's extractor, and the extraction residue was dried with a vacuum dryer until it reached a constant weight to obtain the weight thereof, whereby a difference in weight between the dried residue and the original specimen is calculated.

The first propylene/α-olefin random copolymers of the present invention as illustrated above may be prepared by copolymerizing propylene and α-olefin of 4 - 20 carbon atoms at a temperature of 40 - 100°C so that the structural units (a) derived from propylene are present in an amount of 90 - 99 mol% and the structural units (b) derived from α-olefin are present in an amount of 1 - 10 mol%, in the presence of catalysts formed from

(A) hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

(B) organoaluminum oxy-compounds.

In that case, the copolymerization may be carried out by employing the same conditions as used in the preparation of the aforementioned ethylene copolymers.

The first propylene/α-olefin random copolymers of the present invention are excellent particularly in heat-sealing properties at low temperatures and hence are used as heat-sealing agents.

Hereinafter, the second propylene random copolymers and process for preparing the same of the present invention are illustrated in detail.

The second propylene random copolymers of the invention are random copolymers of propylene, ethylene and α-olefins of 4 - 20 carbon atoms. In the propylene random copolymers, the structural units (a) derived from propylene are present in an amount of 90 - 99 mol%, preferably 92 - 98 mol%, the structural units (b) derived from ethylene in an amount of 0.5 - 9.5 mol%, preferably 1 - 9 mol%, and the structural units (c) derived from α-olefin in an amount of 0.5 - 9.5 mol%, preferably 1 - 9 mol%. If the structural units (a)

derived from propylene present in the said copolymers are less than 90 mol%, the copolymers tend to become poor in anti-blocking properties and stiffness. On the other hand, if the structural units (a) exceed 99 mol%, the copolymers tend to increase in melting point and become poor in heat-sealing properties.

α-olefins of 4 ~ 20 carbon atoms used herein include 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octane, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Among these, particularly preferred is 1-butene.

The second propylene random copolymers of the invention desirably have an intrinsic viscosity [η] as measured in decalin at 135°C of 0.5 ~ 6 dl/g, preferably 1 ~ 5 dl/g. If this intrinsic viscosity is less than 0.5 dl/g, the copolymers tend to become poor in anti-blocking properties and toughness and, on the other hand, if said intrinsic viscosity exceeds 6 dl/g, the copolymers tend to become poor in moldability.

Further, the second propylene/α-olefin random copolymers of the invention have a melting point [Tm] as measured by a differential scanning calorimeter falling within the range of

$$70 < Tm < 155 - 5.5 (100 - P), \text{ preferably}$$

$$90 < Tm < 150 - 5.5 (100 - P)$$

wherein P is the content (mol%) of propylene in the copolymer.

The schematic relationship between the melting point Tm of the above-mentioned propylene random copolymer and the propylene content (mol%) in said copolymer is the same as shown in Fig. 2.

In this manner, the melting point of the second propylene random copolymers is lower by 10 - 20°C than that of the known propylene/α-olefin random copolymers when the amounts of ethylene and α-olefin copolymerized of the former are the same as those of the latter. Accordingly, films obtained from the second propylene random copolymers of the invention are excellent particularly in heat-sealing properties at low temperatures, and the films exhibit excellent heat-sealing properties even when they have small amounts of ethylene and α-olefin copolymerized, and hence they are excellent in anti-blocking properties and have excellent stiffness.

Further, the molecular weight distribution ($\overline{M}w/\overline{M}n$) of the second propylene random copolymers of the invention as obtained by gel permeation chromatography (GPC) is less than 3.5, preferably less than 3.0 and especially less than 2.5. As stated above, the second propylene random copolymers of the invention are narrow in molecular weight distribution

and, from this point, they have excellent anti-blocking properties.

The second propylene random copolymers of the invention are desirably to have a soluble portion in boiling n-pentane in an amount of less than 5% by weight, preferably less than 3% by weight and especially less than 2% by weight.

Furthermore, the second propylene random copolymers of the invention are desirably to have an insoluble portion in boiling trichloroethylene in an amount of less than 5% by weight, preferably less than 3% by weight and especially less than 2% by weight.

The second propylene random copolymers of the present invention as illustrated above may be prepared by copolymerizing propylene, ethylene and α-olefins of 4 - 20 carbon atoms at a temperature of 40 - 100°C so that the structural units (a) derived from propylene are present in an amount of 90 - 99 mol% in the resulting copolymers, the structural units (b) derived from ethylene in an amount of 0.5 - 9.5 mol%, and the structural units (c) derived from α-olefin in an amount of 0.5 - 9.5 mol%, in the presence of catalysts formed from

(A) hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted

groups thereof are linked together via lower alkylene groups, and

[E] organoaluminum oxy-compounds.

In that case, the copolymerization may be carried out by employing the same conditions as used in the preparation of the aforementioned ethylene copolymers.

The second propylene random copolymers of the invention as illustrated above are excellent particularly in heat-sealing properties at low temperatures, and hence are used as heat-sealing agents.

Hereinafter, the first olefin polymerization catalysts of the present invention are illustrated in detail.

The first olefin polymerization catalysts of the invention are formed from

[A] hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B] organoaluminum oxy-compounds, and

[C] organoaluminum compounds.

In the olefin polymerization catalyst mentioned above, the hafnium compounds [A] and organoaluminum oxy-compounds [B] used may be the same as those mentioned previously.

The organoaluminum compounds (C) used herein may be those having in the molecule at least one Al-C bond, for example, the compounds as mentioned below.

That is, (i) organoaluminum compounds represented by the general formula $(R^1)_mAl(OR^2)_nH_pX_q$ wherein R^1 and R^2, which may be the same or different, are each hydrocarbon of usually 1 to 15 carbon atoms, preferably 1 to 10 carbon atoms, X is halogen, m is $1 \leq m \leq 3$, n is $0 \leq n \leq 2$, p is $0 \leq p \leq 2$, and q is $0 \leq q \leq 2$, and $m + n + p + q = 3$, and (ii) alkylated complex compounds of metals of Group 1 of the periodic table and aluminum represented by the general formula $M^1Al(R^1)_4$ wherein M^1 is Li, Na or K, and R^1 is as defined above.

Of the organoaluminum compounds mentioned above, particularly preferred are those having hydrocarbon groups other than n-alkyl group. Hydrocarbon groups other than n-alkyl group may include alkyl having a branched chain such as isoalkyl, cycloalkyl and aryl. The organoaluminum compounds as illustrated above may include, for example, trialkylaluminum such as triisopropylaluminum, triisobutylaluminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum; tricycloalkylaluminum such as tricyclohexylaluminum; triarylaluminum such as

triphenylaluminum and tritolylaluminum; dialkylaluminum hydrides such as diisobutylaluminum hydride; and alkylaluminum alkoxides such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide. Of these organoaluminum compounds, preferred are those having branched alkyl groups, particularly trialkylaluminum compounds. Furthermore, isoprenylaluminum represented by the general formula $(i\text{-}C_5H_9)_xAl_y(C_5H_{10})_z$ wherein x, y and z are each a positive integer, and $z \geq 2x$, is also useful.

Compounds capable of forming the above-mentioned organoaluminum compounds in the polymerization system, for example, halogenated aluminum and alkyl lithium, or halogenated aluminum and alkyl magnesium, may be added to the polymerization system.

In polymerizing olefin by using the first olefin polymerization catalysts of the present invention, the hafnium compound [A] is desirably used in an amount, in terms of hafnium atoms present in the polymerization reaction system, of 10^{-9} - 10^{-2} gram atom/l, preferably 10^{-7} - 10^{-3} gram atom/l, the organoaluminum oxy-compound [B] is desirably used in an amount, in terms of aluminum atoms present in the polymerization reaction system, of less than 3 mg atom/l, preferably 0.01 - 2 mg atom/l and especially 0.02 - 1 mg atom/l, and the organoaluminum compound [C] is desirably used in such an amount that the proportion of aluminum atoms

derived from said organoaluminum compound [C] in the reaction system to the total aluminum atoms of the organoaluminum oxy-compound [B] and organoaluminum compound [C] is 20 - 99%, preferably 25 - 98% and especially 30 - 95%.

In the reaction system, the ratio of the total aluminum atom of the organoaluminum oxy-compound [B] and organoaluminum compound [C] to hafnium atoms of the hafnium compound [A] is usually 20 - 10000, preferably 50 - 5000 and especially 100 - 2000.

The olefin polymerization may be carried out by employing the same condition as used in the preparation of ethylene copolymers as aforesaid.

Hereinafter, the second olefin polymerization catalysts of the present invention are illustrated in detail.

The second olefin polymerization catalysts of the invention are formed from

[A] hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B-1] organoaluminum oxy-compounds formed from tri-n-alkylaluminum, and

[B-2] organoaluminum oxy-compounds in which at least one hydrocarbon group other than n-alkyl is linked to Al atom.

In the olefin polymerization catalysts mentioned above, the hafnium compounds [A] used are the same as those mentioned previously.

The catalyst components [B-1] used in the second olefin polymerization catalysts of the invention are organoaluminum oxy-compounds formed from tri-n-alkylaluminum.

n-alkyl group in the tri-n-alkylaluminum mentioned above includes methyl, ethyl, n-propyl, n-butyl, n-octyl and n-decyl. Among these, particularly preferred is methyl.

The catalyst components [B-2] used in the second olefin polymerization catalysts of the invention are organoaluminum oxy-compounds in which at least one hydrocarbon group other than n-alkyl is linked to Al atom.

The hydrocarbon group other than n-alkyl includes alkyl having branched chain such as isoalkyl, cycloalkyl and aryl.

The above-mentioned organoaluminum oxy-compounds [B-2] in which at least one hydrocarbon group other than n-alkyl is linked to Al atom may be formed from organoaluminum compounds in which at least one hydrocarbon group other than n-alkyl is linked to Al atom. Such organoaluminum compounds as used in the above case include, for example, trialkylaluminum such as triisopropylaluminum, triisobutylaluminum, tri-2-

methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum; tricycloalkylaluminum such as tricyclohexylaluminum; triarylaluminum such as triphenylaluminum and tritolylaluminum; dialkylaluminum hydrides such as diisobutylaluminum hydride; and alkylaluminum alkoxides such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide. Of these organoaluminum compounds, preferred are those having branched alkyl groups, particularly trialkylaluminum compounds. Furthermore, isoprenylaluminum represented by the general formula $(i\text{-}C_4H_9)_xAl_y(C_5H_{10})_z$ wherein x, y and z are each a positive integer, and $z \geq 2x$, is also useful.

In polymerization olefin by using the second olefin polymerization catalysts of the present invention, the hafnium compound [A] is desirably used in an amount, in terms of hafnium atoms present in the polymerization reaction system, of 10^{-8} - 10^{-2} gram atom/l, preferably 10^{-7} - 10^{-3} gram atom/l, the organoaluminum oxy-compound [B-1] in an amount, in terms of aluminum atoms in the polymerization reaction system, of less than 3 mg atom/l, preferably 0.01 - 2 mg atom/l and especially 0.02 - 1 mg atom/l, and the organoaluminum oxy-compound [B-2] in such an amount that the

proportion of aluminum atoms derived from the organoaluminum oxy-compound [B-2] in the reaction system to the total aluminum atom of the organoaluminum oxy-compound [B-1] and organoaluminum oxy-compound [B-2] is 20 - 95%, preferably 25 - 90% and especially 30 - 85%.

In the reaction system, the ration of the total aluminum atom of the organoaluminum oxy-compcund [B-1] and organoaluminum oxy-compound [B-2] to hafnium atoms of the hafnium compound [B] is usually 20 - 10000, preferably 50 - 5000 and especially 100 - 2000.

In that case, the olefin polymerization may be carried out by employing the same conditions as used in the preparation of ethylene copolymers as aforesaid.

EFFECT OF THE INVENTION

Novel ethylene copolymers of the present invention are small in $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, large in MFR_{10}/MFR_2 and excellent in flowability. Accordingly, the ethylene copolymers of the invention have excellent processability and are excellent in anti-blocking properties and the like properties.

Novel propylene copolymers of the invention are low in melting point in comparison with known propylene/α-olefin random copolymers even when said novel propylene copolymers are low in α-olefin content, and hence they have excellent

anti-blocking properties and stiffness. In the present invention, there are also provided processes for preparing these novel copolymers mentioned above readily and efficiently.

The olefin polymerization catalysts of the invention exhibit high activities even when relatively small amounts of organoaluminum oxy-compounds are used therein, and by the use of said catalysts, olefin polymers large in molecular weight and narrow in molecular weight distribution and composition distribution are obtained.

The present invention is illustrated below with reference to examples, but it should be construed that the invention is in no way limited to those examples.

Example 1 (Preparation of ethylene copolymer)

(Preparation of methylaluminoxane)

Methylaluminoxane was prepared in accordance with the procedure described in Polymer Commun., 29, 180 (1988).

(Synthesis of ethylenebis(indenyl)hafnium dichloride)

A nitrogen-purged 200 ml glass flask was charged with 5.4 g of bis(indenyl)ethane [synthesized on the basis of Bull. Soc. Chim., 2954 (1967)] and 50 ml of THF, and the flask was cooled with stirring to -30° ~ -40°C. To the flask was added dropwise 31.5 ml of n-Bu Li (1.6M solution), stirred successively at -30°C for 1 hours, and the temperature was elevated spontaneously to room temperature,

thereby anionizing the bis(indenyl)ethane. Separately, a nitrogen-purged 200 ml glass flask was charged with 60 ml of THF, and the flask was cooled to below -60°C, followed by gradual addition of 6.7 g of $HfCl_4$ (contained 0.78% by weight of zirconium atoms as contaminants). Thereafter, the flask was heated-up to 60°C and stirred for 1 hour. To the flask was added dropwise the anionized ligand, and stirred at 60°C for 2 hours, followed by filtration with a glass filter. The filtrate was concentrated at room temperature to about 1/5 of the original volume. By this operation conducted, solids were separated. The separated solids were filtered with a glass filter, followed by washing with hexane/ethyl ether and vacuum drying to obtain ethylenebis(indenyl)hafnium dichloride.

The hafnium compound thus obtained contained 0.40% by weight of zirconium atoms.

(Polymerization)

A thoroughly nitrogen-purged 2 liter glass flask was charged with 950 ml of toluene and 50 ml of 1-octene, and ethylene gas was passed therethrough at a rate of 160 l/hr. The temperature in the system was elevated to 55°C, and 1.8 mmoles in terms of aluminum atom of methylaluminoxane and 7.5×10^{-3} mmole of ethylenebis(indenyl)hafnium dichloride were added to the system to initiate polymerization. The polymerization was carried out at 60°C for 10 minutes under

atmospheric pressure while continuously feeding ethylene gas. The polymerization was stopped by the addition of small amounts of methanol, and the polymerization solution obtained was poured in large amounts of methanol to separate polymer. The separated polymer was dried at 130°C for 12 hours under reduced pressure to obtain 23.2 g of a polymer having a density of 0.866 g/cm^3, the ethylene content of 81.3 mol%, $[\eta]$ of 1.71 dl/g, $\overline{M}w/\overline{M}n$ of 2.55, MFR_2 of 2.12 g/10 min and MFR_{10}/MFR_2 ratio of 13.1.

Example 2

A thoroughly nitrogen-purged 2 liter glass flask was charged with 1 liter of toluene, and a mixed gas of ethylene and propylene (140 l/hr and 40 l/hr respectively) was passed therethrough. The temperature in the system was elevated to 75°C, and 1.80 mmoles in terms of aluminum atom of methylaluminoxane and 7.5×10^{-3} mmol of ethylenebis(indenyl)hafnium dichloride were added to the system to initiate polymerization. The polymerization was carried out at 80°C for 10 minutes under atmospheric pressure while continuously feeding the above-mentioned mixed gas to the system. Thereafter, the operation was conducted in the same manner as in Example 1 to obtain 17.5 g of a polymer having a density of 0.887 g/cm^3, the ethylene content of 84.0 mol%, $[\eta]$ of 1.50 dl/g, $\overline{M}w/\overline{M}n$ of 2.50, MFR_2 of 0.80 g/10 min and MFR_{10}/MFR_2 ratio of 12.7.

Comparative Example 1

A copolymer of ethylene and propylene (prepared by using a catalyst composed of $VOCl_3$ and aluminum ethyl sesquichloride) having a density of 0.87 g/cm^3, MFR_2 of 2.9 g/10 min and $\overline{Mw}/\overline{Mn}$ of 2.16 was found to have MFR_{10}/MFR_2 ratio of 5.90.

Example 3

(Preparation of hafnium catalyst)

A glass column of 35 mm in inside diameter was filled with a suspension in toluene of 40 g of dimethylsilylated silica gel (Art. 7719, a product of MERCK) dehydrated at room temperature for 4 hours. Subsequently, 200 ml of the toluene solution (Hf = 2.07 m mol/l) of ethylenebis(indenyl)hafnium dichloride prepared in Example 1 was gradually poured into the column. A hafnium solution (Hf = 0.17 m mol/l) eluted by this operation was used as a catalyst component.

(Polymerization)

The polymerization was carried out in the same manner as in Example 1 except that the polymerization was carried out at 70°C for 35 minutes using 6.6×10^{-3} m atom of hafnium atom, to obtain 42.4 g of a colorless transparent polymer having a density of 0.855 g/cm^3, the ethylene content of 75.2 mol%, $[\eta]$ of 1.89 dl/g, $\overline{Mw}/\overline{Mn}$ of 2.48, MFR_2 of 1.49 g/10 min and MFR_{10}/MFR_2 ratio of 10.1.

Example 4

The polymerization was carried out in the same manner as in Example 2 except that the hafnium catalyst component prepared in Example 3 was used in an amount of 6.6×10^{-3} mg atom in terms of hafnium atom to obtain 17.0 g of a colorless transperent polymer having a density of 0.883 g/cm^3, the ethylene content of 83.5 mol%, [η] of 1.61 dl/g, $\overline{M}w/\overline{M}n$ of 2.54, MFR_2 of 0.73 g/10 min, and MFR_{10}/MFR_2 ratio of 12.2.

Example 5

The polymerization was carried out in the same manner as in Example 1 except that the polymerization temperature employed was 40°C and the polymerization time employed was 15 minutes to obtain 20.5 g of a polymer having a density of 0.868 g/cm^3, the ethylene content of 82.0 mol%, [η] of 1.79 dl/g, $\overline{M}w/\overline{M}n$ of 2.81, MFR_2 of 0.90 g/10 min and MFR_{10}/MFR_2 ratio of 32.0.

Example 6 (Preparation of propylene copolymer)

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged at room temperature with 500 ml of toluene, 3 moles of propylene, 0.1 mole of 1-butene and 5 mg atom in terms of Al atom of methylaluminoxane. The temperature in the polymerization system was elevated to 45°C, and 1.25×10^{-3} mmole of the ethylenebis(indenyl)hafnium

dichloride obtained in Example 1 was added to the system to carry out polymerization at 50°C for 0.5 hours. The polymerization was stopped by the addition of methanol to the polymerization system.

The polymer slurry obtained was poured into large amounts of methanol, the slurry was recovered by filtration and washed with an isobutyl alcohol/hydrochloric acid solution to remove the catalyst components therefrom. The recovered slurry was then vacuum dried overnight at 80°C and 200 - 300 mmHg to obtain 27.5 g of a polymer having the 1-butene content of 2.2 mol%, [η] of 3.02 dl/g as measured in decalin at 135°C, a melting point of 124°C as measured by DSC, a boiling trichloroethylene-insoluble content of 0% by weight, boiling n-pentane-soluble content of 0.3% by weight and $\overline{M}w/\overline{M}n$ of 2.41 as measured by GPC.

Example 7

The polymerization was carried out in the same manner as in Example 6 except that the amount of 1-butene charged was changed to 0.25 mol to obtain 29.1 g of a polymer having the 1-butene content of 5.6 mol%, [η] of 2.95 dl/g, a melting point of 116°C, a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 0.4% by weight and $\overline{M}w/\overline{M}n$ of 2.33.

Example 8

(Polymerization)

A mixed gas composed of 96.7 mol% of propylene, 2.1 mol% of 1-butene and 1.2 mol% of ethylene was prepared.

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 500 ml of toluene and then cooled to 0°C, and the autoclave was further charged with 3 moles of the mixed gas prepared above and 5 mg atom in terms of Al atom of methylaluminoxane. The temperature in the polymerization system was elevated to 45°C, and 1.25×10^{-3} m mole of the ethylenebis(indenyl)hafnium dichloride obtained in Example 1 was added to the system to initiate polymerization at 50°C for 0.5 hours. The polymerization was stopped by the addition of methanol to the polymerization system. The polymer slurry obtained was poured into large amounts of methanol, the slurry was recovered by filtration and washed with an isobutyl alcohol/hydrochloric acid solution to remove the catalyst components therefrom. The recovered polymer was then vacuum dried overnight at 80°C and 200 - 300 mmHg to obtain 51.3 g of a polymer having the 1-butene content of 1.4 mol%, the ethylene content of 1.1 mol%, $[\eta]$ of 3.32 dl/g as measured in decalin at 135°C, a melting point of 121°C as measured by DSC, a boiling trichloroethylene-insoluble content of 0% by weight, boiling n-pentane-soluble content of 0.9% by weight and $\bar{M}w/\bar{M}n$ of 2.45 as measured by GPC.

Example 9

The polymerization was carried out in the same manner as in Example 1 except that the mixed gas composed of 95.1 mol% of propylene, 3.9 mol% of 1-butene and 1.0 mol% of ethylene was used to obtain 48.5 g of a polymer having the 1-butene content of 2.7 mol%, the ethylene content of 0.8 mol%, [η] of 3.29 dl/g, a melting point of 118°C, a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 1.1% by weight and $\overline{M}w/\overline{M}n$ of 2.40.

Example 10

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 750 ml of toluene and then saturated with propylene gas. To the autoclave were added 7.5 mg atom in terms of Al atom of methylaluminoxane and 1.80×10^{-3} mmole of the ethylenebis(indenyl)hafnium dichloride. Polymerization was carried out at 50°C for 0.5 hour at the total pressure of 7 kg/cm^2 G while continuously feeding propylene gas to the autoclave. The polymerization was stopped by the addition of methanol to the polymerization system. The polymer slurry obtained was poured into large amounts of methanol, the slurry was recovered by filtration and washed with an isobutyl alcohol/hydrochloric acid

solution to remove the catalyst components therefrom. The recovered slurry was then vacuum dried overnight at 80°C and 200 ~ 300 mmHg to obtain 107.1 g of an isotactic polypropylene having $\overline{M}w/\overline{M}n$ of 1.89 as measured by GPC, a melting point of 132°C as measured by DSC, [η] of 2.82 dl/g as measured in decalin at 135°C, a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.2% by weight.

Example 11

A mixed gas composing 98.5 mol% of propylene gas and 1.5 mol% of ethylene gas was prepared. The operation subsequent thereto was carried out in the same manner as in Example 6 to obtain 53.3 g of a polymer having the ethylene content of 1.3 mol%, [η] of 3.50 dl/g, a melting point of 125°C, a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 1.0% by weight and $\overline{M}w/\overline{M}n$ of 2.39.

Evaluation

Heat-sealing properties of the propylene polymers obtained hereinabove were evaluated in the following manner.

Preparation of film

On a press plate were placed an aluminum sheet of a 0.1 mm thick, a polyester sheet (a product sold under a trade name of Rumilor by Toray) and a polyimide resin sheet (a

product sold under a trade name of Capton by Du Pont), a square of 15 cm × 15 cm of the center of which had been cut off, in that order, and 0.8 g of the specimen was placed in this center (the cut-off portion of the polyimide resin sheet), and then Rumiler®, an aluminum sheet and a press plate were superposed thereon in that order (see Fig. 3).

The specimen thus interposed between the press plates was placed in a hot press kept at 200°C and preheated for about 5 minutes, followed by subjecting three times to pressure application (20 kg/cm² G) and release operation in order to remove air bubbles present in the specimen. Subsequently, the pressure was increased finally to 150 kg/cm² G and the specimen was heated for 5 minutes under pressure. After releasing the pressure, the press plate was taken out from a press machine and transferred to separate press machine kept at 30°C in its press in portion and then cooled for 4 minutes at a pressure of 100 kg/cm², followed by releasing the pressure and taking out the specimen therefrom. Of the films thus obtained, those having a uniform thickness of 50 - 70 μm were used as the films for measurement.

Measurement of heat-sealing strength

The films thus prepared are placed for 2 days in a hygrostat kept at 50°C (aging). In practicing the aging, sheets of paper are applied to both sides of the film so that the films do not come in contact with each other. The films

thus aged are cut up into strips of a 15 mm thick, and two sheets of the strip are placed one upon another and then interposed between two sheets of Teflon Film of a 0.1 mm thick, followed by heat sealing. The heat sealing is carried out while maintaining the temperature of a lower portion of a hot plate of heat sealer constant at 70°C and varying only the temperature of an upper portion of hot plate suitably at intervals of 5°C. The heat-sealing pressure employed is 2 kg/cm^2, the heat-sealing time employed is 1 second, and a width of heat seal is 5 mm (accordingly a sealed area is 15 mm × 5 mm).

Heat-sealing strength is determined by obtaining a peeling strength of the heat sealed film subjected to peeling test at a rate of 30 cm/min at each heat-sealing temperature as mentioned above. (See Fig. 4.)

Following the above-mentioned procedure, a peeling strength at each of the heat-sealing temperatures preset at interval of 5°C is obtained, and the plots of heat-sealing temperature-peeling strength are connected by means of a curved line. On the basis of the curved line, a heat sealing temperature corresponding to a peeling strength of 800 g /15 mm is taken as a completely heat-sealed temperature (see Fig. 5).

Table 1 below shows completely heat-sealed temperatures of the propylene-polymers obtained in the foregoing examples.

Table 1

Example	1	2	3	4	5	6
Completely heat-sealed temperature (°C)	134	125	117	122	120	127

Example 12

(Preparation of organoaluminum oxy-compound [B-1])

A thoroughly nitrogen-purged 400 ml flask was charged with 37 g of $Al_2(SO_4)_3 \cdot 14H_2O$ and 125 ml of toluene and cooled to 0°C, followed by dropwise addition of 500 mmol of trimethylaluminum diluted with 125 ml of toluene. The temperature of the flask was elevated to 40°C, and reaction was continued at that temperature for 10 hours. After the completion of the reaction, solid-liquid separation of the reaction mixture was effected by filtration, and the toluene was removed from the filtrate to obtain 13 g of a white solid organoaluminum oxy-compound. The molecular weight of the compound obtained was 930 as measured in benzene by the cryoscopic method, and n value shown in the catalyst component [B-1] was 14.

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 500 ml of toluene, and the system

was purged with propylene gas. Successively, to the autoclave were added 1 mmol of triisobutylaluminum, 1 mg atom in terms of Al atom of the organoaluminum oxy-compound obtained above, and 1×10^{-3} mmol of the ethylenebis(indenyl)hafnium dichloride obtained in Example 1, and the temperature of the system was elevated to 45°C. Thereafter, polymerization was carried out at 50°C for 1 hours, while feeding propylene gas to the polymerization system so that the total pressure became 7 kg/cm^2 G, to obtain 45.0 g of an isotactic polypropylene having [η] of 2.5 dl/g as measured in decalin at 135°C, $\overline{Mw}/\overline{Mn}$ of 2.2, a melting point of 132°C, a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.2% by weight.

Comparative Example 2

The polymerization of Example 1 was repeated except that the triisobutylaluminum was not used to obtain 5.1 g of isotactic polypropylene having [η] of 1.2 dl/g, $\overline{Mw}/\overline{Mn}$ of 2.1 and a melting point of 131°C.

Example 13

The polymerization of Example 12 was repeated except that in place of the triisobutylaluminum there were used 1 mmol of tri-2-ethylhexylaluminum and 0.5 mg atom in terms of Al atom of commercially available aluminoxane to obtain 38.2

g of isotactic polypropylene having [η] of 2.3 dl/g, $\overline{M}w/\overline{M}n$ of 2.4, a melting point of 131°C, a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.3% by weight.

Example 14

A nitrogen-purged 1 liter glass autoclave was charged with 335 ml of toluene and 15 ml of octene, followed by elevating the temperature of the system to 70°C while blowing ethylene gas thereinto. Successively, to the autoclave were added 0.4 mmol of triisobutylaluminum, 0.2 mg atom in terms of Al atom of commercially available aluminoxane and 3×10^{-3} mmol of the ethylenebis(indenyl)hafnium dichloride obtained in Example 1 to initiate polymerization. The polymerization was carried out at 70°C for 30 minutes while continuously feeding ethylene gas to the polymerization system to obtain 16.8 g of an ethylene/1-octene copolymer having $\overline{M}w/\overline{M}n$ of 3.18, MFR_2 of 0.09 g/10 min, MFR_{10}/MFR_2 of 30.7 and a density of 0.879 g/cm^3.

Example 15

(Preparation of organoaluminum oxy-compound (B-2))

A thoroughly nitrogen-purged 400 ml flask was charged with 4.9 g of $Al_2(SO_4)_3 \cdot 14H_2O$ and 125 ml of toluene and cooled to 0°C, followed by dropwise addition of 200 mmol of triisobutylaluminum diluted with 125 ml of toluene. The

temperature of the reaction system was elevated to 40°C, and reaction was continued at that temperature for 24 hours. After the completion of the reaction, solid-liquid separation of the reaction mixture was conducted by filtration, the toluene was removed from the filtrate, and a molecular weight of the organoaluminum oxy-compound [B-2] obtained was measured in benzene by the cryoscopic method to find that it was 61C.

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 500 ml of toluene, and the system was then purged with propylene gas. Successively, to the autoclave were added 1 mg atom each in terms of Al atom of the organoaluminum oxy-compound [B-1] and the organoaluminum oxy-compound [B-2] and 1.0×10^{-3} mmol of ethylenebis(indenyl)hafnium dichloride, and the temperature of the polymerization system was elevated to 30°C. Thereafter, polymerization was carried out at 30°C for 20 minutes while feeding propylene gas to the total pressure became 5 kg/cm^2 G to obtain 9.5 g of isotactic polypropylene having [η] of 4.1 dl/g, $\overline{M}w/\overline{M}n$ of 3.5, a melting point of 135°C, a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.2% by weight.

Example 16

Example 12 was repeated except that the polymerization was carried out under the total pressure of 7 kg/cm^2 G at 50°C for 1 hours using 1 mg atom in terms of Al atom of (iso-C_4H_9)$_2$Al-O-Al(iso-C_4H_9)$_2$ as the organoaluminum oxy-compound [B-2] and 0.5 mg atom in terms of Al atom of the organoaluminum oxy-compound [B-1] to obtain 35.1 g of isotactic polypropylene having [η] of 7.2 dl/g, Mw/Mn of 2.1, a melting point of 132°C, a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.3% by weight.

Comparative Example 1

Example 16 was repeated except that the organoaluminum oxy-compound [B-2] was not used to obtain 2.4 g of isotactic polypropylene having [η] of 1.5 dl/g and a melting point of 130°C.

Example 17

A thoroughly nitrogen-purged 1 liter glass autoclave was charged with 328 ml of toluene and 22 ml of 1-octane, and the system was then elevated in temperature to 70°C while blowing ethylene gas thereinto. Successively, to the autoclave were added 0.4 mg atom in terms of Al atom of (iso-C_4H_9)$_2$Al-(O-Al)$_2$-OAl(iso-C_4H_9)$_2$ as the organoaluminum oxy-compound [B-2],

iso-C_4H_9

0.2 mg atom in terms of Al atom of the above-mentioned organoaluminum oxy-compound [B-1] and 3×10^{-3} mmol of ethylenebis(indenyl)hafnium dichloride to initiate polymerization. The polymerization was carried out at 70°C for 30 minutes while continuously feeding ethylene gas to the polymerization system to obtain 12.3 g of an ethylene/1-octene copolymer having $\overline{Mw}/\overline{Mn}$ of 2.49, MFR_2 of 7.2 g/10 min, MFR_{10}/MFR_2 of 9.3 and a density of 0.853 g/cm^3.

What is claimed is:

1. In ethylene copolymers composed of structural units (a) derived from ethylene and structural units (b) derived from α-olefin of 3 - 20 carbon atoms, the improvement which resides in that the ethylene copolymers have

(A) a density of 0.85 - 0.92 g/cm^3,

(B) an intrinsic viscosity [η] as measured in decalin at 135°C of 0.1 - 10 dl/g,

(C) a ratio ($\overline{M}w/\overline{M}n$) of a weight average molecular weight ($\overline{M}w$) to a number average molecular weight ($\overline{M}n$) as measured by GPC of 1.2 - 4, and

(D) a ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg at 190°C of 8 - 50.

2. In a process for preparing ethylene copolymers, the improvement which comprises copolymerizing ethylene and α-olefin of 3 - 20 carbon atoms in the presence of a catalyst so that the resulting copolymers have a density of 0.85 - 0.92 g/cm^3, said catalyst being composed of

(A) a hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among indenyl groups or substituted groups thereof are linked together via lower alkylene groups or hafnium compounds obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel, and

(B) an organoaluminum oxy-compound.

3. In propylene random copolymers composed of structural units (a) derived from propylene and structural units (b) derived from α-olefin of 4 - 20 carbon atoms, the improvement which resides in that the propylene random copolymers have

(i) the structural units (a) in an amount of 90 - 99 mol% and the structural units (b) in an amount of 1 - 10 mol%,

(ii) an intrinsic viscosity [η] as measured in decalin at 135°C of 0.5 - 6 dl/g,

(iii) a melting point [Tm] as measured by a differential scanning calorimeter falling within the range of

$$90 < Tm < 155 - 3.5\,(100 - P)$$

wherein P is the propylene content (mol%) present in the copolymer,

(iv) a ratio ($\overline{M}w/\overline{M}n$) of a weight average molecular weight ($\overline{M}w$) to a number average molecular weight ($\overline{M}n$) as measured by gel permeation chromatography of less than 3.5, and

(v) a boiling trichloroethylene-insoluble content of less than 5% by weight.

4. In a process for preparing propylene random copolymers, the improvement which comprises copolymerizing propylene and α-olefin of 4 - 20 carbon atoms at a temperature of 40 - 200°C in the presence of a catalyst so that the resulting

copolymers have structural units (a) derived from propylene in an amount of 90 - 99 mol% and structural units (b) derived from α-olefin in an amount of 1 - 10 mol%, said catalyst being formed from

(A) a hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

(B) an organoaluminum oxy-compound.

5. In propylene random copolymers composed of structural units (a) derived from propylene, structural units (b) derived from ethylene and structural units (c) derived from α-olefin of 4 - 20 carbon atoms, the improvement which resides in that the propylene random copolymers have

(i) the structural units (a) in an amount of 90 - 99 mol%, the structural units (b) in an amount of 0.5 - 9.5 mol% and the structural units (c) in an amount of 0.5 - 9.5 mol%,

(ii) an intrinsic viscosity [η] as measured in decalin at 135°C of 0.5 - 6 dl/g,

(iii) a melting point [Tm] as measured by a differential scanning calorimeter falling with in the range of

$70 < Tm < 135 - 5.5 (100 - P)$

wherein P is the propylene content (mol%) present in the copolymer, and

(iv) a boiling trichloroethylene-insoluble content of less than 5% by weight.

6. In a process for preparing propylene random copolymers, the improvement which comprises copolymerizing propylene, ethylene and α-olefin of 4 - 20 carbon atoms in the presence of a catalyst so that the resulting copolymers have structural units (a) derived from propylene in an amount 90 - 99 mol%, structural units (b) derived from ethylene in an amount of 0.5 - 9.5 mol% and structural units (c) derived from α-olefin in an amount of 0.5 - 9.5 mol%, said catalyst being formed from

[A] a hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

[B] an organoaluminum oxy-compound.

7. A heat sealing agent comprising the propylene random copolymers as claimed in claim 3 or 5.

8. An olefin polymerization catalyst formed from

[A] a hafnium compound having as a ligand a multidentate compound in which at least two groups selected from

among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B] an organoaluminum oxy-compound, and

[C] an organoaluminum compound.

9. An olefin polymerization catalyst formed from

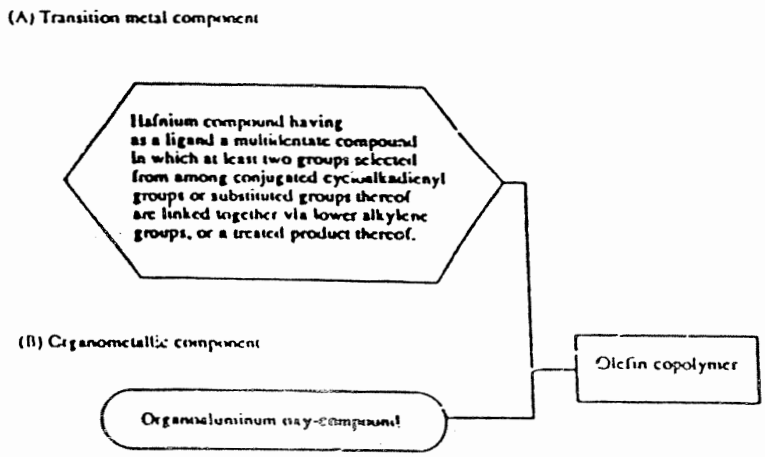
[A] a hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B] an organoaluminum oxy-compound formed from tri-n-alkylaluminum, and

[C] an organoaluminum oxy-compound in which at least one hydrocarbon group other than n-alkyl group has been linked to Al atom.

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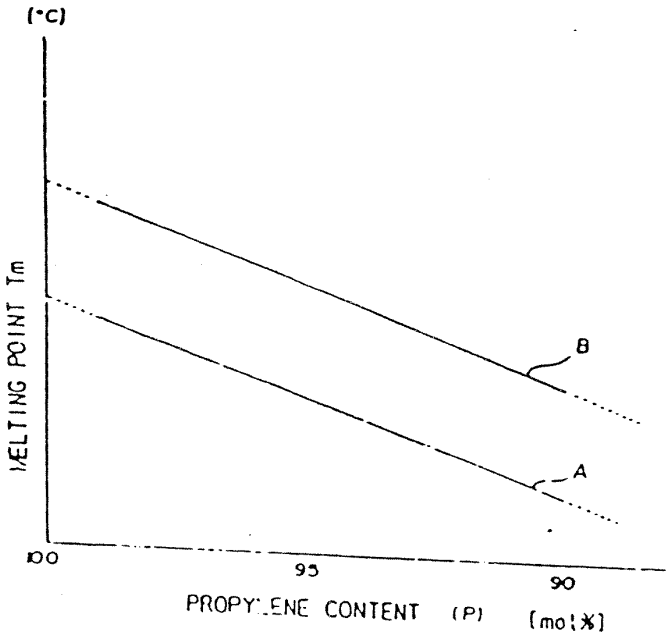
FIG. 1



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FIG.2



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FIG.3

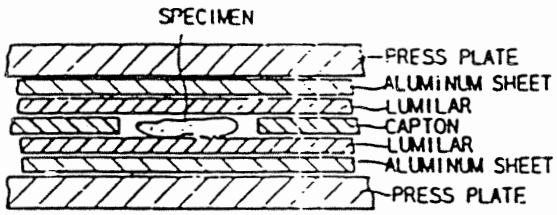
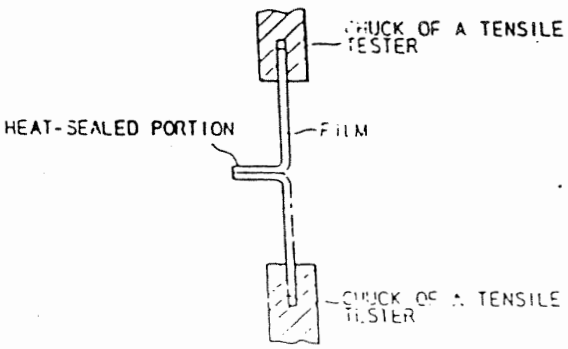


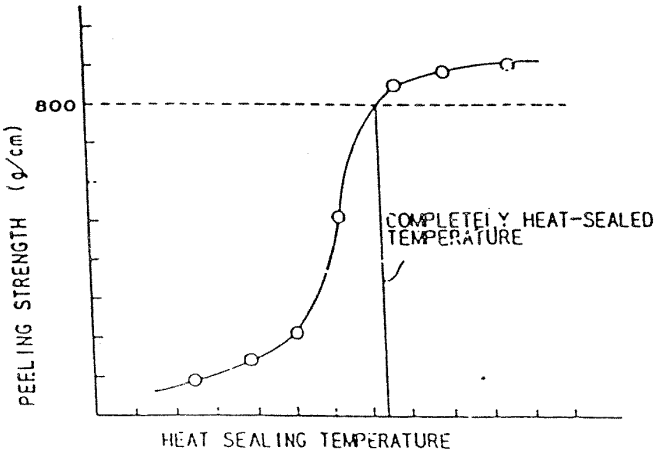
FIG.4



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FIG.5



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