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(54) **Szilárd titán-katalizátor komponens, katalizátor olefin-polimerizációhoz, és eljárás olefin-polimer előállítására**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

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(54) **SOLID TITANIUM CATALYST COMPONENT, CATALYST FOR OLEFIN POLYMERIZATION, AND PROCESS FOR PRODUCING OLEFIN POLYMER**

FESTE TITANKATALYSATOR-KOMPONENTE, KATALYSATOR FÜR DIE  
OLEFINPOLYMERISATION UND VERFAHREN ZUR HERSTELLUNG VON OLEFINPOLYMER

COMPOSANT CATALYSEUR AU TITANE SOLIDE, CATALYSEUR POUR LA POLYMERISATION  
D'OLEFINES ET PROCEDE DE PRODUCTION DE POLYMERES D'OLEFINES

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(56) References cited:  
**JP-A- 06 122 716 JP-A- 2001 114 811**  
**JP-A- 2003 040 918 US-A- 4 725 656**

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## Description

## TECHNICAL FIELD

5 **[0001]** The present invention relates to a solid titanium catalyst component which is preferably used for polymerization of an  $\alpha$ -olefin having 3 or more carbon atoms, to a catalyst for olefin polymerization containing the solid titanium catalyst component, and to a process for producing an olefin polymer using the catalyst for olefin polymerization.

## BACKGROUND ART

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**[0002]** As the catalysts for producing an olefin polymer such as a homopolymer of ethylene or an  $\alpha$ -olefin, and a copolymer of ethylene and an  $\alpha$ -olefin, the catalysts containing a titanium compound supported on magnesium halide in the active state have been conventionally known (hereinafter, the term "polymerization" may be described to encompass both of "homopolymerization" and "copolymerization").

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**[0003]** As the catalyst for olefin polymerization, a catalyst containing titanium tetrachloride or titanium trichloride, which is called a Ziegler-Natta catalyst, a catalyst composed of a solid titanium catalyst component comprising magnesium, titanium, halogen and an electron donor, and an organometallic compound, and the like have been widely known.

**[0004]** The latter catalyst exhibits high activity in the polymerization of  $\alpha$ -olefins such as propylene and butene-1, in addition to ethylene. Also, the obtained  $\alpha$ -olefin polymer may have high stereoregularity.

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**[0005]** It is reported that when among these catalysts, in particular, a catalyst comprising a solid titanium catalyst component having an electron donor, supported thereon, selected from carboxylic acid esters, typically exemplified by phthalic acid esters, and as a co-catalyst component, an aluminum-alkyl compound, and a silicon compound having at least one Si-OR (wherein R is a hydrocarbon group) is used, excellent polymerization activity and stereospecificity are exhibited in JP-A No. 57-63310 (Patent Document 1), etc.

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**[0006]** The obtained polymers obtained by using the above-described catalyst often have narrower molecular weight distributions, as compared with the polymers obtained by using a Ziegler-Natta catalyst. It is known that the polymers having narrow molecular weight distributions tend to have "low melt flowability", "low melt tension", "poor moldability", "slightly low rigidity", or the like. On the other hand, from the standpoints of improvement of productivity, reduction in cost, or the like, various high speed molding technologies such as, for example, high speed stretching technologies aimed at improvement of productivity of the stretched film, have evolved.

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**[0007]** When the polymers having relatively narrow molecular weight distributions as described above are to be stretched at a high speed, for example, the neck-in or flapping of the films may become more remarkable due to shortage of melt tension, and thus it becomes difficult to improve the productivity. Therefore, the polymers having higher melt tensions are demanded by the market.

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**[0008]** In order to solve these problems, there have been many reports on a method for broadening the molecular weight distributions of the polymers by producing the polymers having different molecular weights by means of a multi-stage polymerization (JP-A No. 5-170843 (Patent Document 2)), a catalyst comprising plural kinds of electron donors (JP-A No. 3-7703 (Patent Document 3)), a catalyst using a succinic acid ester having an asymmetric carbon as the electron donor contained in the solid titanium catalyst component (pamphlet of International Publication WO 01/057099 (Patent Document 4), pamphlet of International Publication WO 00/63261 (Patent Document 5), pamphlet of International Publication WO 02/30998 (Patent Document 6)), and the like.

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**[0009]** On the other hand, JP-A No. 2001-114811 (Patent Document 7) and JP-A No. 2003-40918 (Patent Document 8) disclose a solid catalyst component for olefin(s) polymerization, which is obtained by bringing into contact with a titanium compound, a magnesium compound and an electron-donating compound, and a catalyst for olefin(s) polymerization comprising the catalyst component. As the electron-donating compound, 1, 2-cyclohexanedicarboxylic acid esters having a purity of the trans-isomers of 80% or more are used in the invention as described in Patent Document 7; and cyclohexenedicarboxylic acid diesters are used in the invention as described in Patent Document 8. As the specific example of these cyclohexenedicarboxylic acid diesters, 1-cyclohexenedicarboxylic acid diester only is disclosed, in which the alkoxy carbonyl group is bonded to the 1-position and the 2-position of the cyclohexene ring of 1-cyclohexene (paragraphs [0021] to [0024], and Examples). However, Patent Documents 7 and 8 have no description on the molecular weight distributions of the olefin polymers.

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**[0010]** US 4,725,656 (Patent Document 9) discloses a catalyst component for use in preparing polymer products having an improved melt index. The catalyst component comprises magnesium, titanium, halogen and an electron donor. The electron donor is a non-aromatic cyclic polycarboxylic acid. The cyclic polycarboxylic acid has one or more double bonds within the cyclic backbone, or a heteroatom within the cyclic backbone, or both. The carboxylic acids are provided at the 1- and 2-positions of the non-aromatic cyclic ring. The non-aromatic cyclic ring may be further substituted.

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[Patent Document 1] JP-A No. 57-63310

[Patent Document 2] JP-A No. 5-170843  
 [Patent Document 3] JP-A No. 3-7703  
 [Patent Document 4] Pamphlet of International Publication WO 01/057099  
 [Patent Document 5] Pamphlet of International Publication WO 00/63261  
 5 [Patent Document 6] Pamphlet of International Publication WO 02/30998  
 [Patent Document 7] JP-A No. 2001-114811  
 [Patent Document 8] JP-A No. 2003-40918  
 [Patent Document 9] US 4,725,656

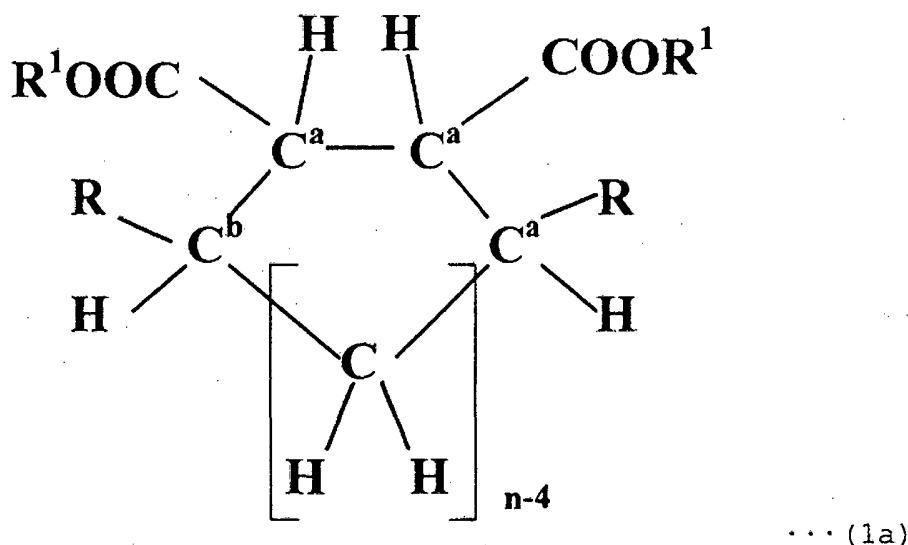
10 DISCLOSURE OF THE INVENTION

[0011] However, the above-described catalyst has been the catalysts which have an insufficient effect of broadening the molecular weight distribution of the olefin polymer, and according to the investigation conducted by the present inventors, broaden the molecular weight distribution by increasing the content of the low molecular weight components.  
 15 On the other hand, as evaluated from the market, it cannot be said that the catalysts provide sufficient improvement of the melt tension of the olefin polymer. Further, from the viewpoint of reduction in the cost, appearance of a catalyst which makes it possible to produce an olefin polymer having a molecular weight distribution broadened by means of a simpler process is demanded by the market.

[0012] Therefore, it is an object of the present invention to provide a catalyst component and a catalyst which are capable of conveniently producing an olefin polymer having a broad molecular weight distribution and a high melt tension, and being suitable for high speed stretch and high speed molding.

[0013] The present inventors have made extensive studies, and as a result, they found that by using a solid titanium catalyst component comprising a specific cyclic ester compound having a plurality of carboxylic acid ester groups, an olefin polymer having a broad molecular weight distribution can be prepared, thus completing the invention. In addition,  
 25 Patent Documents 7 and 8 have neither description nor disclosure on a cyclic ester compound (a) having a substituent R, represented by the following formula (1a).

[0014] The solid titanium catalyst component (I) of the invention is characterized in that it comprises titanium, magnesium, halogen, and a cyclic ester compound (a) specified by the following formula (1a) :



wherein n is an integer of 5 to 10;

50 a plurality of R<sup>1</sup>'s are each independently a monovalent hydrocarbon group having 1 to 20 carbon atoms;  
 a plurality of R's are each independently an atom or group selected from a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a halogen atom, a nitrogen-containing group, an oxygen-containing group, a phosphorus-containing group, a halogen-containing group and a silicon-containing group, or they may be bonded to each other to form a ring, but at least one of R's is not a hydrogen atom; and  
 55 in the case where two C<sup>a</sup>'s are contained in the backbone of the ring, the backbone of the ring have 5 to 10 carbon atoms.

[0015] In the formula (1a) the bonds between the carbon atoms in the cyclic backbone are all single bonds.

[0016] In the formula (1a), it is preferable that the cyclic backbone has 6 carbon atoms.

[0017] The solid titanium catalyst component (I) of the invention may further comprise an aromatic carboxylic acid ester and/or a compound having two or more ether linkages through a plurality of carbon atoms.

5 [0018] The catalyst for olefin polymerization of the invention is characterized in that it comprises the solid titanium catalyst component (I) and an organometallic compound catalyst component (II) containing a metal element selected from Groups I, II and XIII of the periodic table.

[0019] The catalyst for olefin polymerization of the invention may further comprise an electron donor (III).

[0020] The process for producing an olefin polymer of the invention is characterized in that it comprises polymerizing an olefin in the presence of the catalyst for olefin polymerization.

10 [0021] The solid titanium catalyst component, the catalyst for olefin polymerization and the process for producing an olefin polymer of the invention are suitable for producing an olefin polymer having high stereoregularity and broad molecular weight distribution with high activity.

15 [0022] Further, when the solid titanium catalyst component, the catalyst for olefin polymerization and the process for producing an olefin polymer of the invention are used, it can be expected that an olefin polymer, for example, having excellent rigidity, as well as the molding properties such as high speed stretchability and high speed moldability can be prepared.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 [0023] Hereinbelow, the solid titanium catalyst component (I), the catalyst for olefin polymerization and the process for producing an olefin polymer according to the invention will be described in detail.

##### [Solid titanium catalyst component (I)]

25 [0024] The solid titanium catalyst component (I) according to the invention is characterized in that it comprises titanium, magnesium, halogen, and a cyclic ester compound (a).

##### <Cyclic ester compound (a)>

30 [0025] The above-described cyclic ester compound (a) comprises a plurality of carboxylic acid ester groups, and is represented by formula (1a), as set out in the Disclosure of the Invention.

[0026] In the formula (1a), n is an integer of 5 to 10, preferably an integer of 5 to 7, and particularly preferably 6. Further, C<sup>a</sup> and C<sup>b</sup> represent carbon atoms.

[0027] The bonds between the carbon atoms in the cyclic backbone are all single bonds.

35 [0028] A plurality of R<sup>1</sup>'s are each independently a monovalent hydrocarbon group having 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, more preferably 2 to 8 carbon atoms, even more preferably 4 to 8 carbon atoms, and particularly preferably 4 to 6 carbon atoms. Examples of these hydrocarbon groups include an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl group, a decyl group, a dodecyl group, a tetradecyl group, a hexadecyl group, an octadecyl group, an eicosyl group, and the like; and among them, preferred are an n-butyl group, an isobutyl group, a hexyl group and an octyl group, and more preferred are an n-butyl group and an isobutyl group.

40 [0029] A plurality of R's are each independently an atom or group selected from a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a halogen atom, a nitrogen-containing group, an oxygen-containing group, a phosphorus-containing group, a halogen-containing group and a silicon-containing group, but at least one of R's is not a hydrogen atom.

45 [0030] As the R which is not a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms is preferred, and examples of this hydrocarbon group having 1 to 20 carbon atoms include aliphatic, alicyclic or aromatic hydrocarbons such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, an n-pentyl group, a cyclopentyl group, an n-hexyl group, a cyclohexyl group, a vinyl group, a phenyl group and an octyl group. Among them, preferred is an aliphatic hydrocarbon group, and specifically preferred are a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group and a sec-butyl group.

50 [0031] Further, R's may be bonded to each other to form a ring. In the case where two C<sup>a</sup>'s bonded with COOR<sup>1</sup> are contained in the backbone of the ring, the backbone of the ring have 5 to 10 carbon atoms.

55 [0032] Examples of the backbone of the ring include a norbornane backbone, or the like.

[0033] Further, a plurality of R's may be a carbonyl structure-containing group such as a carboxylic acid ester group, an alkoxy group, a siloxy group, an aldehyde group and an acetyl group, and it is preferable that these substituents contain one or more hydrocarbon groups.

diethyl 4-methylcyclohexane-1,3-dicarboxylate,  
diisobutyl 4-methylcyclohexane-1,3-dicarboxylate,  
diethyl 4-methylcyclohexane-1,2-dicarboxylate,  
di-n-propyl 4-methylcyclohexane-1,2-dicarboxylate,  
5 diisopropyl 4-methylcyclohexane-1,2-dicarboxylate,  
di-n-butyl 4-methylcyclohexane-1,2-dicarboxylate,  
diisobutyl 4-methylcyclohexane-1,2-dicarboxylate,  
dihexyl 4-methylcyclohexane-1,2-dicarboxylate,  
diheptyl 4-methylcyclohexane-1,2-dicarboxylate,  
10 dioctyl 4-methylcyclohexane-1,2-dicarboxylate,  
di-2-ethylhexyl 4-methylcyclohexane-1,2-dicarboxylate,  
didecyl 4-methylcyclohexane-1,2-dicarboxylate,  
diethyl 5-methylcyclohexane-1,3-dicarboxylate,  
diisobutyl 5-methylcyclohexane-1,3-dicarboxylate,  
15 diethyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
di-n-propyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
diisopropyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
di-n-butyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
diisobutyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
20 dihexyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
diheptyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
dioctyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
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didecyl 3,4-dimethylcyclohexane-1,2-dicarboxylate,  
25 diethyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
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diisopropyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
di-n-butyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
diisobutyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
30 dihexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
diheptyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
dioctyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
di-2-ethylhexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
didecyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
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diisopropyl 3,6-diphenylcyclohexane-1,2-dicarboxylate,  
di-n-butyl 3,6-diphenylcyclohexane-1,2-dicarboxylate,  
diisobutyl 3,6-diphenylcyclohexane-1,2-dicarboxylate,  
40 dihexyl 3,6-diphenylcyclohexane-1,2-dicarboxylate,  
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diisobutyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
dihexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
diheptyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
50 dioctyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl  
3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
didecyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
diethyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
di-n-propyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
55 diisopropyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
di-n-butyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
diisobutyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
dihexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,

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diheptyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
dioctyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl  
3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
5 didecyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
diethyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, di-n-propyl  
3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diisopropyl  
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3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diisobutyl  
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dioctyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate,  
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diheptyl 3-methylcyclopentane-1,2-dicarboxylate,  
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diisobutyl 4-methylcyclopentane-1,2-dicarboxylate,  
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diheptyl 4-methylcycloheptane-1,2-dicarboxylate,

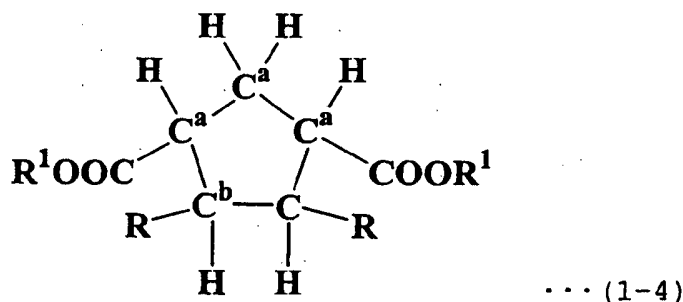
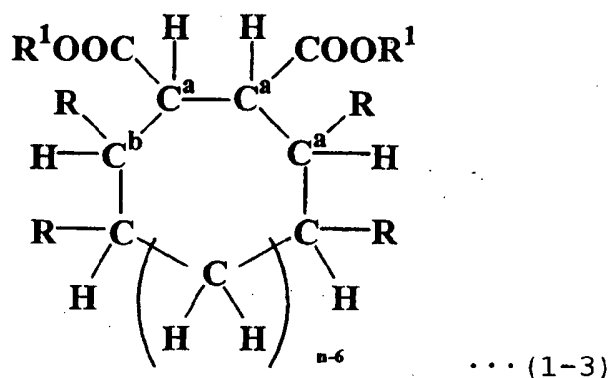
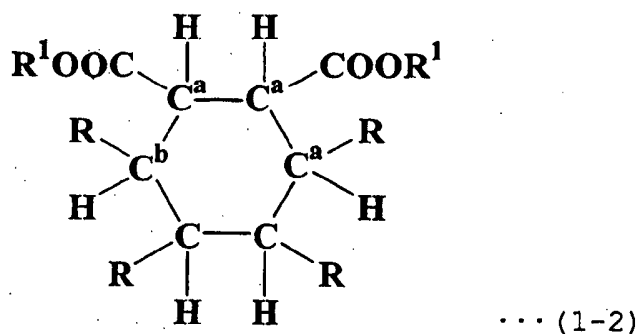
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 diethyl 5-methylcycloheptane-1,3-dicarboxylate,  
 diisobutyl 5-methylcycloheptane-1,3-dicarboxylate,  
 diethyl 3,4-dimethylcycloheptane-1,2-dicarboxylate,  
 5 diisobutyl 3,4-dimethylcycloheptane-1,2-dicarboxylate,  
 diheptyl 3,4-dimethylcycloheptane-1,2-dicarboxylate,  
 didecyl 3,4-dimethylcycloheptane-1,2-dicarboxylate,  
 diethyl 3,7-dimethylcycloheptane-1,2-dicarboxylate,  
 diisobutyl 3,7-dimethylcycloheptane-1,2-dicarboxylate,  
 10 diheptyl 3,7-dimethylcycloheptane-1,2-dicarboxylate,  
 didecyl 3,7-dimethylcycloheptane-1,2-dicarboxylate,  
 diethyl 3-hexylcycloheptane-1,2-dicarboxylate,  
 diethyl 3,7-dihexylcycloheptane-1,2-dicarboxylate,  
 diisobutyl 3-hexyl-7-pentylcycloheptane-1,2-dicarboxylate,  
 15 diethyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 di-n-propyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 diisopropyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 di-n-butyl  
 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 20 diisobutyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 dihexyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 dioctyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 didecyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 diethyl 3-methylcyclooctane-1,2-dicarboxylate,  
 25 diethyl 3-methylcyclodecane-1,2-dicarboxylate,  
 isobutyl 3-vinylcyclohexane-1,2-dicarboxylate,  
 isobutyl 3,6-diphenylcyclohexane-1,2-dicarboxylate,  
 ethyl 3,6-dicyclohexylcyclohexane-1,2-dicarboxylate,  
 diisobutyl norbornane-2,3-dicarboxylate,  
 30 diisobutyl tetracyclododecane-2,3-dicarboxylate,  
 diethyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 di-n-propyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 diisopropyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 di-n-butyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 35 diisobutyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 dihexyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 diheptyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 dioctyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 di-2-ethylhexyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 40 didecyl 3-methyl-4-cyclohexene-1,2-dicarboxylate,  
 diethyl 4-methyl-4-cyclohexene-1,3-dicarboxylate,  
 diisobutyl 4-methyl-4-cyclohexene-1,3-dicarboxylate,  
 diethyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 di-n-propyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 45 diisopropyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 di-n-butyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 diisobutyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 dihexyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 diheptyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 50 dioctyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 di-2-ethylhexyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 didecyl 4-methyl-4-cyclohexene-1,2-dicarboxylate,  
 diethyl 5-methyl-4-cyclohexene-1,3-dicarboxylate,  
 diisobutyl 5-methyl-4-cyclohexene-1,3-dicarboxylate,  
 55 diethyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
 di-n-propyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
 diisopropyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
 di-n-butyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,

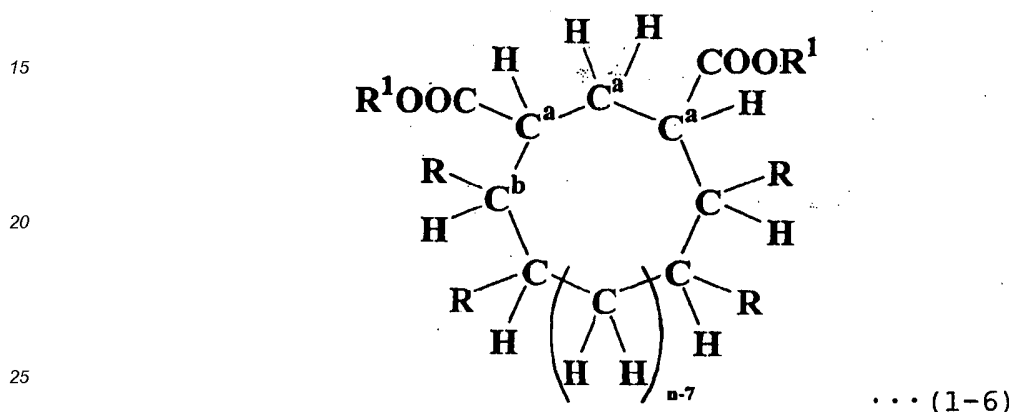
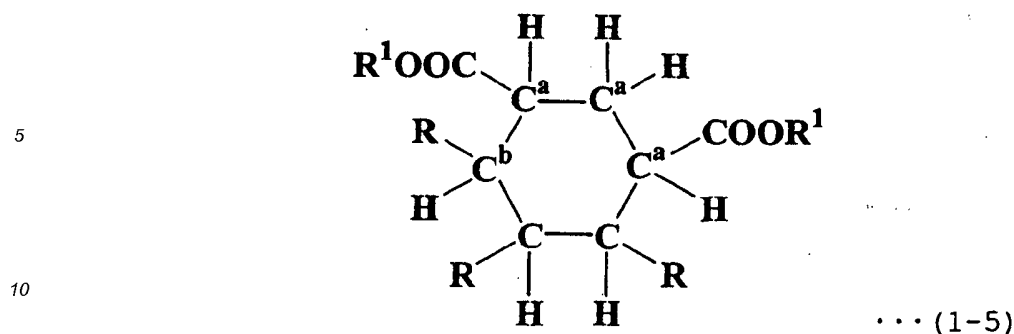


diisobutyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
dihexyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
diheptyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
dioctyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
5 di-2-ethylhexyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
didecyl 3,4-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
diethyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
di-n-propyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
diisopropyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
10 di-n-butyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
diisobutyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
dihexyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
diheptyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
dioctyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
15 di-2-ethylhexyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
didecyl 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate,  
diethyl 3-hexyl-4-cyclohexene-1,2-dicarboxylate,  
diisobutyl 3-hexyl-4-cyclohexene-1,2-dicarboxylate,  
diethyl 3,6-dihexyl-4-cyclohexene-1,2-dicarboxylate,  
20 diisobutyl 3-hexyl-6-pentyl-4-cyclohexene-1,2-dicarboxylate,  
diethyl 3-methyl-3-cyclopentene-1,2-dicarboxylate,  
diisobutyl 3-methyl-3-cyclopentene-1,2-dicarboxylate,  
diheptyl 3-methyl-3-cyclopentene-1,2-dicarboxylate,  
didecyl 3-methyl-3-cyclopentene-1,2-dicarboxylate,  
25 diethyl 4-methyl-3-cyclopentene-1,3-dicarboxylate,  
diisobutyl 4-methyl-3-cyclopentene-1,3-dicarboxylate,  
diethyl 4-methyl-3-cyclopentene-1,2-dicarboxylate,  
diisobutyl 4-methyl-3-cyclopentene-1,2-dicarboxylate,  
diheptyl 4-methyl-3-cyclopentene-1,2-dicarboxylate,  
30 didecyl 4-methyl-3-cyclopentene-1,2-dicarboxylate,  
diethyl 5-methyl-3-cyclopentene-1,3-dicarboxylate,  
diisobutyl 5-methyl-3-cyclopentene-1,3-dicarboxylate,  
diethyl 3,4-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
diisobutyl 3,4-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
35 diheptyl 3,4-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
didecyl 3,4-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
diethyl 3,5-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
diisobutyl 3,5-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
diheptyl 3,5-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
40 didecyl 3,5-dimethyl-3-cyclopentene-1,2-dicarboxylate,  
diethyl 3-hexyl-3-cyclopentene-1,2-dicarboxylate,  
diethyl 3,5-dihexyl-3-cyclopentene-1,2-dicarboxylate,  
diisobutyl 3-hexyl-5-pentyl-3-cyclopentene-1,2-dicarboxylate,  
diethyl 3-methyl-4-cycloheptene-1,2-dicarboxylate,  
45 diisobutyl 3-methyl-4-cycloheptene-1,2-dicarboxylate,  
diheptyl 3-methyl-4-cycloheptene-1,2-dicarboxylate,  
didecyl 3-methyl-4-cycloheptene-1,2-dicarboxylate,  
diethyl 4-methyl-4-cycloheptene-1,3-dicarboxylate,  
diisobutyl 4-methyl-4-cycloheptene-1,3-dicarboxylate,  
50 diethyl 4-methyl-4-cycloheptene-1,2-dicarboxylate,  
diisobutyl 4-methyl-4-cycloheptene-1,2-dicarboxylate,  
diheptyl 4-methyl-4-cycloheptene-1,2-dicarboxylate,  
didecyl 4-methyl-4-cycloheptene-1,2-dicarboxylate,  
diethyl 5-methyl-4-cycloheptene-1,3-dicarboxylate,  
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diethyl 3,4-dimethyl-4-cycloheptene-1,2-dicarboxylate,  
diisobutyl 3,4-dimethyl-4-cycloheptene-1,2-dicarboxylate,  
diheptyl 3,4-dimethyl-4-cycloheptene-1,2-dicarboxylate,

didecyl 3,4-dimethyl-4-cycloheptene-1,2-dicarboxylate,  
 diethyl 3,7-dimethyl-4-cycloheptene-1,2-dicarboxylate,  
 diisobutyl 3,7-dimethyl-4-cycloheptene-1,2-dicarboxylate,  
 diheptyl 3,7-dimethyl-4-cycloheptene-1,2-dicarboxylate,  
 5 didecyl 3,7-dimethyl-4-cycloheptene-1,2-dicarboxylate,  
 diethyl 3-hexyl-4-cycloheptene-1,2-dicarboxylate,  
 diethyl 3,7-dihexyl-4-cycloheptene-1,2-dicarboxylate,  
 diisobutyl 3-hexyl-7-pentyl-4-cycloheptene-1,2-dicarboxylate,  
 diethyl 3-methyl-5-cyclooctene-1,2-dicarboxylate,  
 10 diethyl 3-methyl-6-cyclodecene-1,2-dicarboxylate,  
 isobutyl 3-vinyl-4-cyclohexene-1,2-dicarboxylate,  
 isobutyl 3,6-diphenyl-4-cyclohexene-1,2-dicarboxylate,  
 ethyl 3,6-dicyclohexyl-4-cyclohexene-1,2-dicarboxylate,

15 **[0034]** The compounds having the diester structure s described above may exist in the form of a cis- or trans-isomer derived from a plurality of the COOR<sup>1</sup> groups in the formula (1a), either of which has effects complying with the purpose of the invention, but the compounds having higher content of the trans-isomers are preferred. The compounds having higher content of the trans-isomers have the effects of broadening the molecular weight distribution, as well as tend to have higher activity, and higher stereoregularity of the obtained polymer.





wherein in the formulas (1-1) to (1-6), R<sup>1</sup> and R have the same meanings as above;

in the formulas (1-1) to (1-3), a single bond (excluding C<sup>a</sup>-C<sup>a</sup> bonds and a C<sup>a</sup>-C<sup>b</sup> bond) in the cyclic backbone may be replaced with a double bond;

in the formulas (1-4) to (1-6), a single bond (excluding C<sup>a</sup>-C<sup>a</sup> bonds) in the cyclic backbone may be replaced with a double bond; and

in the formulas (1-3) and (1-6), n is an integer of 7 to 10.

**[0035]** As the cyclic ester compound (a), particularly preferable are the compounds represented by the following formula (1a):

Specific examples of the compounds represented by the formula (1a) include

40 diisobutyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
 di-n-octyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
 diisobutyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
 45 diisobutyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate,  
 diisobutyl 3,6-diethylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3,6-diethylcyclohexane-1,2-dicarboxylate,  
 50 di-n-octyl 3,6-diethylcyclohexane-1,2-dicarboxylate,  
 diisobutyl 3,5-dimethylcyclopentane-1,2-dicarboxylate,  
 di-n-hexyl 3,5-dimethylcyclopentane-1,2-dicarboxylate,  
 di-n-octyl 3,5-dimethylcyclopentane-1,2-dicarboxylate,  
 diisobutyl 3-methyl-5-ethylcyclopentane-1,2-dicarboxylate,  
 55 di-n-hexyl 3-methyl-5-ethylcyclopentane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-5-ethylcyclopentane-1,2-dicarboxylate,  
 di-n-hexyl 3-methyl-5-n-propylcyclopentane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-5-n-propylcyclopentane-1,2-dicarboxylate,

diisobutyl 3,5-diethylcyclopentane-1,2-dicarboxylate,  
 di-n-hexyl 3,5-diethylcyclopentane-1,2-dicarboxylate,  
 di-n-octyl 3,5-diethylcyclopentane-1,2-dicarboxylate,  
 diisobutyl 3,7-dimethylcycloheptane-1,2-dicarboxylate,  
 di-n-hexyl 3,7-dimethylcycloheptane-1,2-dicarboxylate,  
 di-n-octyl 3,7-dimethylcycloheptane-1,2-dicarboxylate,  
 diisobutyl 3-methyl-7-ethylcycloheptane-1,2-dicarboxylate,  
 di-n-hexyl 3-methyl-7-ethylcycloheptane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-7-ethylcycloheptane-1,2-dicarboxylate,  
 di-n-hexyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-7-n-propylcycloheptane-1,2-dicarboxylate,  
 diisobutyl 3,7-diethylcycloheptane-1,2-dicarboxylate,  
 di-n-hexyl 3,7-diethylcycloheptane-1,2-dicarboxylate,  
 di-n-octyl 3,7-diethylcycloheptane-1,2-dicarboxylate,

and the like.

Among these compounds, preferred are

diisobutyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
 di-n-octyl 3,6-dimethylcyclohexane-1,2-dicarboxylate,  
 diisobutyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate,  
 diisobutyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate,  
 di-n-octyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate,  
 diisobutyl 3,6-diethylcyclohexane-1,2-dicarboxylate,  
 di-n-hexyl 3,6-diethylcyclohexane-1,2-dicarboxylate, and  
 di-n-octyl 3,6-diethylcyclohexane-1,2-dicarboxylate.

**[0036]** The reason for this is that these compounds have high catalytic performances, and can be prepared using a Diels Alder reaction at a relatively low cost.

**[0037]** These compounds may be used alone or in combination of two or more kinds thereof. Further, these cyclic ester compounds (a) may be used in combination with a catalyst component (b) or a catalyst component (c) as described below, as long as it does not give any adverse effect on the purpose of the invention.

**[0038]** Further, the cyclic ester compound (a) may be formed during the process of producing the solid titanium catalyst component (I). For example, when the solid titanium catalyst component (I) is produced, the cyclic ester compound (a) can be contained in the solid titanium catalyst component by involving a process of substantially bringing an anhydrous carboxylic acid or carboxylic acid dihalide corresponding to a catalyst component (a), and a corresponding alcohol into contact with each other.

**[0039]** By the process for producing an olefin polymer of the invention, a polymer having a broad molecular weight distribution can be obtained. The reason for this is unclear at present, but is assumed to be as follows.

**[0040]** It is known that the cyclic hydrocarbon structures form a variety of steric structures such as a chair conformation and a boat conformation. In addition, when the cyclic structure has a substituent, variation of the steric structure which can be taken further increases. If the bond between a carbon atom bonded with an ester group (COOR<sup>1</sup> group) and another carbon atom bonded with an ester group (COOR<sup>1</sup> group) among the carbon atoms constituting the cyclic backbone of the cyclic ester compound (a) is a single bond, variation of the steric structure which can be taken increases. These various steric structures which can be taken lead to the formation of various active species on the solid titanium catalyst component (I). As a result, when the olefin polymerization is carried out by using the solid titanium catalyst component (I), the olefin polymers having various molecular weights can be prepared at one time, that is, the olefin polymers having broad molecular weight distributions can be prepared.

**[0041]** For the production of the solid titanium catalyst component (I) of the invention, a magnesium compound and a titanium compound are used, in addition to the cyclic ester compound (a).

<Magnesium compound>

**[0042]** Specific examples of the magnesium compound include well-known magnesium compounds including

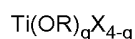
magnesium halides such as magnesium chloride and magnesium bromide;  
 alkoxy magnesium halides such as methoxymagnesium chloride, ethoxymagnesium chloride and phenoxymagnesium chloride;  
 alkoxy magnesium such as ethoxymagnesium, isopropoxymagnesium, butoxymagnesium and 2-ethylhexoxymagnesium;  
 aryloxymagnesiums such as phenoxymagnesium;  
 magnesium carboxylates such as magnesium stearate;  
 and the like.

**[0043]** These magnesium compounds may be used alone or in combination of two or more kinds thereof. Further, these magnesium compounds may be in the form of a complex compound or a composite compound with other metals, or in the form of a mixture with other metal compounds.

**[0044]** Among these, halogen-containing magnesium compounds are preferred, and magnesium halide, in particular magnesium chloride is preferably used. In addition, alkoxy magnesium such as ethoxymagnesium is also preferably used. Further, the magnesium compounds may be those derived from other materials, for example, those obtained by bringing an organomagnesium compound such as a Grignard reagent, and titanium halide, silicon halide, alcohol halide, and the like into contact with each other.

<Titanium compound>

**[0045]** Examples of the titanium compound include a tetravalent titanium compound represented by the following formula:



(wherein R is a hydrocarbon group, X is a halogen atom, and g satisfies the condition  $0 \leq g \leq 4$ ). More specifically, examples thereof include

titanium tetrahalides such as  $\text{TiCl}_4$  and  $\text{TiBr}_4$ ;  
 alkoxytitanium trihalides such as  $\text{Ti(OCH}_3)_2\text{Cl}_2$ ,  $\text{Ti(OC}_2\text{H}_5)_2\text{Cl}_2$ ,  $\text{Ti(O-n-C}_4\text{H}_9)_2\text{Cl}_2$ ,  $\text{Ti(OC}_2\text{H}_5)_2\text{Br}_2$  and  $\text{Ti(O-iso-C}_4\text{H}_9)_2\text{Br}_2$ ;  
 alkoxytitanium dihalides such as  $\text{Ti(OCH}_3)_3\text{Cl}$ ,  $\text{Ti(OC}_2\text{H}_5)_3\text{Cl}$  and  $\text{Ti(OC}_2\text{H}_5)_3\text{Br}$ ;  
 alkoxytitanium monohalides such as  $\text{Ti(OCH}_3)_4$ ,  $\text{Ti(OC}_2\text{H}_5)_4$ ,  $\text{Ti(O-n-C}_4\text{H}_9)_4$  and  $\text{Ti(O-2-ethylhexyl)}_4$ ;  
 and the like.

**[0046]** Among these, preferred are titanium tetrahalides, and particularly preferred is titanium tetrachloride. These titanium compounds can be used alone or in combination of two or more kinds thereof.

**[0047]** Examples of the magnesium compounds and the titanium compounds include those as described in detail in the above-described Patent Document 1, Patent Document 2, or the like.

**[0048]** For the production of the solid titanium catalyst component (I) of the invention, a well-known method can be employed without limit except that the cyclic ester compound (a) is used. Specific preferable examples of the process include the following processes (P-1) to (P-4).

(P-1) Process of bringing a solid adduct comprising of a magnesium compound and a catalyst component (b), a cyclic ester compound (a) and a liquid-state titanium compound into contact with each other in a suspended state in the coexistence of an inert hydrocarbon solvent.

(P-2) Process of bringing a solid adduct comprising of a magnesium compound and a catalyst component (b), a cyclic ester compound (a) and a liquid-state titanium compound into contact with each other in plural steps.

(P-3) Process of bringing a solid adduct comprising of a magnesium compound and a catalyst component (b), a cyclic ester compound (a) and a liquid-state titanium compound into contact with each other in a suspended state in the coexistence of an inert hydrocarbon solvent, and in plural steps.

(P-4) Process of bringing a liquid-state magnesium compound comprising of a magnesium compound and a catalyst component (b), a liquid-state titanium compound and a cyclic ester compound (a) into contact with each other.

**[0049]** The reaction temperature for the production of the solid titanium catalyst component (I) is in the range of preferably  $-30^\circ\text{C}$  to  $150^\circ\text{C}$ , more preferably  $-25^\circ\text{C}$  to  $130^\circ\text{C}$ , and even more preferably  $-25^\circ\text{C}$  to  $120^\circ\text{C}$ .

**[0050]** Further, the production of the solid titanium catalyst component can be carried out, if necessary, in the presence of a well-known medium. Examples of the medium include the compounds of aromatic hydrocarbons such as toluene having some polarity, well-known aliphatic hydrocarbons or alicyclic hydrocarbons such as heptane, octane, decane and cyclohexane, and among these, aliphatic hydrocarbons are preferably exemplified.

**[0051]** When the olefin polymerization reaction is carried out by using the solid titanium catalyst component (I) prepared

within the above-described range, the effect of obtaining a polymer having a broad molecular weight distribution can be highly compatibilized with activity of the catalyst and high stereoregularity of the obtained polymer.

(Catalyst component (b))

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**[0052]** For the catalyst component (b) used for the formation of the above-described solid adduct or liquid-state magnesium compound, preferred are well-known compounds which can solubilize the magnesium compound in the temperature range of room temperature to around 300°C, and preferred are, for example, alcohols, aldehydes, amines, carboxylic acids and a mixture thereof. Examples of these compounds include those as described in detail in the above-

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described Patent Document 1 or Patent Document 2.

**[0053]** More specific examples of alcohols having ability to solubilize the magnesium compound include aliphatic alcohols such as methanol, ethanol, propanol, butanol, isobutanol, ethylene glycol, 2-methylpentanol, 2-ethylbutanol, n-heptanol, n-octanol, 2-ethylhexanol, decanol and dodecanol;

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alicyclic alcohols such as cyclohexanol and methylcyclohexanol;  
aromatic alcohols such as benzyl alcohol and methylbenzyl alcohol;  
aliphatic alcohols having an alkoxy group such as n-butyl cellosolve;  
and the like.

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**[0054]** Examples of the carboxylic acids include organic carboxylic acids having at least 7 carbon atoms, such as caprylic acid and 2-ethylhexanoic acid. Examples of the aldehydes include aldehydes having at least 7 carbon atoms, such as capric aldehyde and 2-ethylhexyl aldehyde.

**[0055]** Examples of the amines include amines having at least 6 carbon atoms, such as heptylamine, octylamine, nonylamine, laurylamine and 2-ethylhexylamine.

**[0056]** As the catalyst component (b), preferred are the above-described alcohols, and particularly preferred are ethanol, propanol, butanol, isobutanol, hexanol, 2-ethylhexanol, decanol and the like.

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**[0057]** The amounts of the magnesium compound and the catalyst component (b) to be used in the production of the solid adduct or liquid-state magnesium compound vary depending on the kinds thereof, the contact conditions, or the like, but the magnesium compound is used in an amount of 0.1 to 20 mol/liter, and preferably 0.5 to 5 mol/liter per unit volume of the catalyst component (b). Further, if desired, a medium which is inert to the solid adduct can be used in combination. Preferable examples of the medium include well-known hydrocarbon compounds such as heptane, octane and decane.

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**[0058]** The compositional ratio of magnesium of the obtained solid adduct or liquid-state magnesium compound to the catalyst component (b) varies depending on the kinds of the compound to be used, and thus it cannot be generally defined. But the amount of the catalyst component (b) is in the range of preferably 2.6 moles or more, and more preferably 2.7 moles or more and 5 moles or less, based on 1 mole of magnesium in the magnesium compound.

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Aromatic carboxylic acid ester and/or compound having two or more ether linkages through a plurality of carbon atoms

**[0059]** The solid titanium catalyst component (I) of the invention may further comprise an aromatic carboxylic acid ester and/or a compound having two or more ether linkages through a plurality of carbon atoms (hereinafter, also referred to as the "catalyst component (c)"). When the solid titanium catalyst component (I) of the invention contains the catalyst component (c), activity and stereoregularity may be increased or the molecular weight distribution may be further broadened.

40

**[0060]** As this catalyst component (c), well-known aromatic carboxylic acid esters or polyether compounds, which are preferably used for the conventionally used catalysts for olefin polymerization, for example, those as described in the above-described Patent Document 2, JP-A No. 2001-354714, or the like can be used without limit.

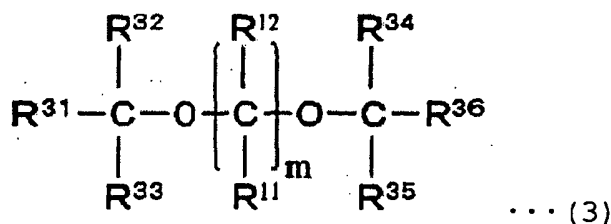
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**[0061]** Specific examples of this aromatic carboxylic acid ester include aromatic polyvalent carboxylic acid esters such as phthalic acid ester, in addition to aromatic carboxylic acid monoesters such as benzoic acid ester and toluic acid ester. Among these, preferred are aromatic polyvalent carboxylic acid esters, and more preferred are phthalic acid esters. As these phthalic acid esters, preferred are phthalic acid alkyl esters such as ethyl phthalate, n-butyl phthalate, isobutyl phthalate, hexyl phthalate and heptyl phthalate, and particularly preferred is isobutyl phthalate.

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**[0062]** Further, more specific examples of the polyether compounds include the compounds represented by the following formula (3):

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10 **[0063]** Further, in the above formula (3),  $m$  is an integer satisfying the condition  $1 \leq m \leq 10$ , and preferably an integer satisfying the condition  $3 \leq m \leq 10$ , and  $\text{R}^{11}$  to  $\text{R}^{36}$  are each independently a hydrogen atom or substituents having at least one kind of element selected from carbon, hydrogen, oxygen, fluorine, chlorine, bromine, iodine, nitrogen, sulfur, phosphorus, boron and silicon.

15 **[0064]** When  $m$  is 2 or more, a plurality of  $\text{R}^{11}$  and  $\text{R}^{12}$  may be the same or different from each other. Any of  $\text{R}^{11}$  to  $\text{R}^{36}$ , and preferably  $\text{R}^{11}$  and  $\text{R}^{12}$  may be bonded to each other to form a ring other than a benzene ring.

**[0065]** Specific examples of some of these compounds include monosubstituted dialkoxypropanes such as

2-isopropyl-1,3-dimethoxypropane,  
2-s-butyl-1,3-dimethoxypropane, and  
2-cumyl-1,3-dimethoxypropane;  
disubstituted dialkoxypropanes such as  
2-isopropyl-2-isobutyl-1,3-dimethoxypropane,  
2,2-dicyclohexyl-1,3-dimethoxypropane,  
2-methyl-2-isopropyl-1,3-dimethoxypropane,  
2-methyl-2-cyclohexyl-1,3-dimethoxypropane,  
2-methyl-2-isobutyl-1,3-dimethoxypropane,  
2,2-diisobutyl-1,3-dimethoxypropane,  
2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-diethoxypropane,  
2,2-diisobutyl-1,3-dibutoxypropane,  
2,2-di-s-butyl-1,3-dimethoxypropane,  
2,2-dineopentyl-1,3-dimethoxypropane,  
2-isopropyl-2-isopentyl-1,3-dimethoxypropane and  
2-cyclohexyl-2-cyclohexylmethyl-1,3-dimethoxypropane;  
dialkoxyalkanes such as 2,3-dicyclohexyl-1,4-diethoxybutane,  
2,3-dicyclohexyl-1,4-diethoxybutane,  
2,3-diisopropyl-1,4-diethoxybutane,  
2,4-diphenyl-1,5-dimethoxypentane,  
2,5-diphenyl-1,5-dimethoxyhexane,  
2,4-diisopropyl-1,5-dimethoxypentane,  
2,4-diisobutyl-1,5-dimethoxypentane and  
2,4-diisoamyl-1,5-dimethoxypentane;  
trialkoxyalkanes such as  
2-methyl-2-methoxymethyl-1,3-dimethoxypropane,  
2-cyclohexyl-2-ethoxymethyl-1,3-diethoxypropane and  
2-cyclohexyl-2-methoxymethyl-1,3-dimethoxypropane;  
dialkoxyalkanes such as  
2,2-diisobutyl-1,3-dimethoxy-4-cyclohexene,  
2-isopropyl-2-isoamyl-1,3-dimethoxy-4-cyclohexene,  
2-cyclohexyl-2-methoxymethyl-1,3-dimethoxy-4-cyclohexene,  
2-isopropyl-2-methoxymethyl-1,3-dimethoxy-4-cyclohexene,  
2-isobutyl-2-methoxymethyl-1,3-dimethoxy-4-cyclohexene,  
2-cyclohexyl-2-ethoxymethyl-1,3-dimethoxy-4-cyclohexene,  
2-isopropyl-2-ethoxymethyl-1,3-dimethoxy-4-cyclohexene and  
2-isobutyl-2-ethoxymethyl-1,3-dimethoxy-4-cyclohexene;

55 and the like.

**[0066]** Among these, preferred are 1,3-diethers, and particularly preferred are

2-isopropyl-2-isobutyl-1,3-dimethoxypropane,  
 2,2-diisobutyl-1,3-dimethoxypropane,  
 2-isopropyl-2-isopentyl-1,3-dimethoxypropane,  
 2,2-dicyclohexyl-1,3-dimethoxypropane and  
 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane.

**[0067]** These compounds may be used alone or in combination of two or more kinds thereof.

**[0068]** The cyclic ester compound (a), the catalyst component (b) and the catalyst component (c) as described above may well be thought to belong to the components which are referred to as electron donors by a skilled person in the art. It is known that the electron donor components have the effect of enhancing stereoregularity of the obtained polymer, the effect of controlling the composition distribution of the obtained copolymer and the effect as an aggregator of controlling the particle shape and particle size of the catalyst particle, while maintaining high activity of the catalyst.

**[0069]** It is thought that the cyclic ester compound (a) also exhibits the effect of controlling the molecular weight distribution because it itself is an electron donor.

**[0070]** For the solid titanium catalyst (I) of the invention, the halogen/titanium (atomic ratio) (i.e., number of moles of the halogen atoms/number of moles of the titanium atoms) is preferably 2 to 100, and more preferably 4 to 90; the cyclic ester compound (a)/titanium (molar ratio) (i.e., number of moles of the cyclic ester compound (a))/number of moles of the titanium atoms) is preferably 0.01 to 100, and more preferably 0.2 to 10; and as for the catalyst component (b) and the catalyst component (c), the catalyst component (b)/the titanium atom (molar ratio) is preferably 0 to 100, and more preferably 0 to 10, and the catalyst component (c)/the titanium atom (molar ratio) is preferably 0 to 100, and more preferably 0 to 10.

**[0071]** The magnesium/titanium (atomic ratio) (i.e., number of moles of the magnesium atoms/number of moles of the titanium atoms) is preferably 2 to 100, and more preferably 4 to 50.

**[0072]** The contents of the components which may be contained in addition to the cyclic ester compound (a), for example, the catalyst component (b) and the catalyst component (c) are 20% by weight or less, and preferably 10% by weight or less, based on 100% by weight of the cyclic ester compound (a).

**[0073]** As the more specific production conditions of the solid titanium catalyst component (I), the conditions as described in, for example, EP 585869 A1 (European patent application publication No. 0585869.), the above-described Patent Document 2, or the like can be preferably employed, except that the cyclic ester compound (a) is used.

#### [Catalyst for olefin polymerization]

**[0074]** The catalyst for olefin polymerization according to the invention is characterized in that it comprises the solid titanium catalyst component (I) according to the invention and an organometallic compound catalyst component (II) containing a metal element selected from Groups I, II and XIII of the periodic table.

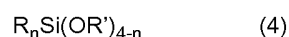
#### <Organometallic compound catalyst component (II)>

**[0075]** For the organometallic compound catalyst component (II), a compound containing a metal in Group XIII, for example, an organoaluminum compound and a complex alkylate of a metal in Group I and aluminum, an organometallic compound of a metal in Group II, or the like can be used. Among these, preferred is the organoaluminum compound.

**[0076]** Specific preferable examples of the organometallic compound catalyst component (II) include the organometallic compound catalyst components as described in well-known documents, for example, the above-described EP 585869 A1.

#### <Catalyst component (III)>

**[0077]** The catalyst for olefin polymerization of the invention, if necessary, may comprise the above-described catalyst component (III) together with the organometallic compound catalyst component (II). Preferable examples of the catalyst component (III) include organosilicon compounds. Examples of these organosilicon compounds include the compound represented by the following general formula (4):



wherein R and R' are hydrocarbon groups, and n is an integer satisfying the condition  $0 < n < 4$ .

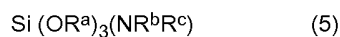
**[0078]** As the organosilicon compounds represented by the above formula (4), specifically diisopropyldimethoxysilane, t-butylmethylmethoxydimethoxysilane, t-butylmethylmethoxydiethoxysilane, t-amylmethylmethoxydiethoxysilane, dicyclohexyldimethoxysilane, cyclohexylmethylmethoxydimethoxysilane, cyclohexylmethylmethoxydiethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, t-butyltriethoxysilane, phenyltriethoxysilane, cyclohexyltrimethoxysilane, cyclopentyltrimethoxysilane, 2-methylcyclopentyltri-



methoxysilane, cyclopentyltriethoxysilane, dicyclopentylmethoxysilane, dicyclopentylmethoxydimethoxysilane, dicyclopentylmethoxydiethoxysilane, tricyclopentylmethoxysilane, dicyclopentylmethylmethoxysilane, dicyclopentylethylmethoxysilane, cyclopentylmethoxydimethoxysilane, or the like is used.

**[0079]** Among these, vinyltriethoxysilane, diphenyldimethoxysilane, dicyclohexyldimethoxysilane, cyclohexylmethyl-  
5 dimethoxysilane or dicyclopentylmethoxydimethoxysilane is preferably used.

**[0080]** Also, preferable examples of the above-described organosilicon compounds further include the silane compounds represented by the following formula (5) as described in the pamphlet of International Publication WO 2004/016662.



**[0081]** In the formula (5),  $\text{R}^a$  is a hydrocarbon group having 1 to 6 carbon atoms, and examples of  $\text{R}^a$  include an unsaturated or saturated aliphatic hydrocarbon group having 1 to 6 carbon atoms, or the like, and particularly preferably a hydrocarbon group having 2 to 6 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, an  
15 n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, an n-pentyl group, an isopentyl group, a cyclopentyl group, an n-hexyl group, a cyclohexyl group, and the like, among which an ethyl group is particularly preferable.

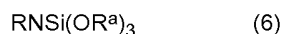
**[0082]** In the formula (5),  $\text{R}^b$  is a hydrocarbon group having 1 to 12 carbon atoms or a hydrogen atom, and examples of  $\text{R}^b$  include an unsaturated or saturated aliphatic hydrocarbon group having 1 to 12 carbon atoms, a hydrogen atom, and the like. Specific examples thereof include a hydrogen atom, a methyl group, an ethyl group, an n-propyl group, an  
20 isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, an n-pentyl group, an isopentyl group, a cyclopentyl group, an n-hexyl group, a cyclohexyl group, an octyl group, and the like, among which an ethyl group is particularly preferable.

**[0083]** In the formula (5),  $\text{R}^c$  is a hydrocarbon group having 1 to 12 carbon atoms, and examples of  $\text{R}^c$  include an unsaturated or saturated aliphatic hydrocarbon group having 1 to 12 carbon atoms, a hydrogen atom, and the like. Specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl  
25 group, an isobutyl group, a sec-butyl group, an n-pentyl group, an isopentyl group, a cyclopentyl group, an n-hexyl group, a cyclohexyl group, an octyl group, and the like, among which an ethyl group is particularly preferable.

**[0084]** Specific examples of the compound represented by the formula (5) include

30 dimethylaminotriethoxysilane,  
diethylaminotriethoxysilane,  
diethylaminotrimethoxysilane,  
diethylaminotriethoxysilane,  
35 diethylaminotri-n-propoxysilane,  
di-n-propylaminotriethoxysilane,  
methyl-n-propylaminotriethoxysilane,  
t-butylaminotriethoxysilane,  
ethyl-n-propylaminotriethoxysilane,  
40 ethyl-isopropylaminotriethoxysilane and  
methylethylaminotriethoxysilane.

**[0085]** Further, other examples of the above-described organosilicon compounds include the compound represented by the following formula (6):



**[0086]** In the formula (6), RN is a cyclic amino group, and examples of the cyclic amino group include a perhydroquinolino group, a perhydroisoquinolino group, a 1,2,3,4-tetrahydroquinolino group, a 1,2,3,4-tetrahydroisoquinolino group, an  
50 octamethyleneimino group, and the like. Specific examples of the compound represented by the above formula (6) include (perhydroquinolino)triethoxysilane, (perhydroisoquinolino)triethoxysilane, (1,2,3,4-tetrahydroquinolino)triethoxysilane, (1,2,3,4-tetrahydroisoquinolino)triethoxysilane, octamethyleneiminotriethoxysilane, and the like.

**[0087]** These organosilicon compounds may be used in combination of two or more kinds thereof.

**[0088]** Further, other preferable examples of the compounds which are useful as the catalyst component (III) include  
55 polyether compounds which are exemplified as the aromatic carboxylic acid ester and/or the compound having two or more ether linkages through a plurality of carbon atoms (the catalyst component (c)).

**[0089]** Among these polyether compounds, preferred are 1,3-diethers, and particularly preferred is 2-isopropyl-2-isobutyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane,

2,2-dicyclohexyl-1,3-dimethoxypropane and 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane.

**[0090]** These compounds may be used alone or in combination of two or more kinds thereof.

**[0091]** Further, the catalyst for olefin polymerization of the invention may further comprise other components useful for olefin polymerization, if necessary, in addition to each of the above-described components. Examples of such other components include a support such as silica, an antistatic agent, a particle coagulant, a preservation stabilizing agent, and the like.

[Process for producing olefin polymer]

**[0092]** The process for producing an olefin polymer according to the invention is characterized in that it comprises polymerizing an olefin by using the catalyst for olefin polymerization of the invention. In the invention, the term "polymerization" may encompass copolymerization such as random copolymerization and block copolymerization, as well as homopolymerization.

**[0093]** For the process for producing an olefin polymer of the invention, it is also possible that polymerization is carried out in the presence of a prepolymerization catalyst obtained by prepolymerization of an  $\alpha$ -olefin in the presence of the catalyst for olefin polymerization of the invention. This prepolymerization is carried out by prepolymerization of an  $\alpha$ -olefin in an amount of 0.1 to 1000 g, preferably 0.3 to 500 g, and particularly preferably 1 to 200 g, based on 1 g of the catalyst for olefin polymerization.

**[0094]** The concentration of the catalyst in the prepolymerization system may be higher than that in the polymerization system.

**[0095]** In the prepolymerization, the concentration of the solid titanium catalyst component (I) is in the range of preferably about 0.001 to 200 mmol, more preferably about 0.01 to 50 mmol, and particularly preferably 0.1 to 20 mmol, in terms of titanium atom, based on 1 liter of the liquid medium.

**[0096]** In the prepolymerization, the amount of the organometallic compound catalyst component (II) may be such that 0.1 to 1,000 g, and preferably 0.3 to 500 g of the polymer is produced, based on 1 g of the solid titanium catalyst component (I), and the amount is preferably about 0.1 to 300 mol, more preferably about 0.5 to 100 mol, and particularly preferably 1 to 50 mol, based on 1 mol of the titanium atom in the solid titanium catalyst component (I).

**[0097]** In the prepolymerization, the catalyst component (III) may be used, if necessary, and these components are used in an amount of 0.1 to 50 mol, preferably 0.5 to 30 mol, and particularly preferably 1 to 10 mol, based on 1 mol of the titanium atom in the solid titanium catalyst component (I).

**[0098]** The prepolymerization can be carried out under the mild condition by adding an olefin and the above-described catalyst components to an inert hydrocarbon medium.

**[0099]** In this case, specific examples of the inert hydrocarbon medium to be used include aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosene;

alicyclic hydrocarbons such as cycloheptane, cycloheptane, methylcycloheptane, 4-cycloheptane, 4-cycloheptane and methyl-4-cycloheptane;

aromatic hydrocarbons such as benzene, toluene and xylene;

halogenated hydrocarbons such as ethylene chloride and chlorobenzene;

and a mixture thereof.

**[0100]** Among these inert hydrocarbon media, aliphatic hydrocarbons are particularly preferably used. As such, when the inert hydrocarbon medium is used, it is preferable that the prepolymerization is carried out batchwise.

**[0101]** On the other hand, the prepolymerization may be carried out by using olefin itself as a solvent, and substantially without a solvent. In this case, it is preferable that the prepolymerization is carried out continuously.

**[0102]** The olefins used in the prepolymerization may be the same or different from those used in the polymerization as described below, and specifically, it is preferably propylene.

**[0103]** The temperature for prepolymerization is in the range of preferably about -20 to +100°C, more preferably about -20 to +80°C, and even more preferably 0 to +40°C.

**[0104]** Next, the polymerization after the afore-mentioned prepolymerization or without prepolymerization will be described.

**[0105]** Examples of the olefins which can be used (that is, polymerized) for the polymerization include  $\alpha$ -olefins having 3 to 20 carbon atoms, for example, linear olefins such as propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; and branched olefins such as 4-methyl-1-pentene, 3-methyl-1-pentene and 3-methyl-1-butene, and preferred are propylene, 1-butene, 1-pentene and 4-methyl-1-pentene. Further, particularly preferred are propylene, 1-butene and 4-methyl-1-pentene, from the viewpoint that the polymer having a broader molecular weight distribution easily exhibits its advantages for the resin with high rigidity.

**[0106]** Along with these  $\alpha$ -olefins, ethylene; aromatic vinyl compounds such as styrene and allylbenzene; or alicyclic vinyl compounds such as vinylcyclohexane and vinylcycloheptane can be used. Furthermore, the compound having a polyunsaturated bond such as, for example, conjugated dienes or nonconjugated dienes, for example, dienes such as

cyclopentene, cycloheptene, norbornene, tetracyclododecene, isoprene and butadiene can be used as the polymerization materials together with ethylene and an  $\alpha$ -olefin. These compounds may be used alone or in combination of two or more kinds thereof. (Hereinafter, ethylene or the olefins to be used together with the " $\alpha$ -olefin having 3 to 20 carbon atoms" may be also referred to as "other olefins").

5 [0107] Among such other olefins, preferred are ethylene and the aromatic vinyl compounds. Further, small amount, for example, 10% by weight or less, and preferably 5% by weight, based on 100% by weight of the total amount of olefins, of the other olefins such as ethylene may be used in combination therewith.

[0108] According to the invention, the prepolymerization and the polymerization can be carried out in any of liquid phase polymerizations such as bulk polymerization, solution polymerization and suspension polymerization, and vapor phase polymerization.

10 [0109] When slurry polymerization is employed for the polymerization, the inert hydrocarbons used in the prepolymerization as described above, or an olefin which is liquid at a reaction temperature can be used as a reaction solvent.

[0110] In the polymerization in the process for producing the polymer of the invention, the above-described solid titanium catalyst component (I) is used in an amount of usually about 0.0001 to 0.5 mmol, and preferably about 0.005 to 0.1 mmol, in terms of titanium atom, based on 1 liter of the polymerization volume. Further, the above-described organometallic compound catalyst component (II) is used in an amount of usually about 1 to 2000 mol, and preferably about 5 to 500 mol, in terms of titanium atom in the prepolymerization catalyst component in the polymerization system. The above-described catalyst component (III), if used, is used in an amount of 0.001 to 50 mol, preferably 0.01 to 30 mol, and particularly preferably 0.05 to 20 mol in the organometallic compound catalyst component (II).

20 [0111] If the polymerization is carried out in the presence of hydrogen, the molecular weight of the obtained polymer can be controlled to obtain a polymer with a high melt flow rate.

[0112] In the polymerization according to the invention, the polymerization temperature of olefins is in the range of usually about 20 to 200°C, preferably about 30 to 100°C, and more preferably about 50 to 90°C. The pressure is set to be in the range of usually ambient pressure to 100 kgf/cm<sup>2</sup> (9.8 MPa), and preferably about 2 to 50 kgf/cm<sup>2</sup> (0.20 to 4.9 MPa). In the process for producing a polymer of the invention, the polymerization can be carried out by any of batchwise, semi-continuous and continuous processes. Further, the polymerization can be carried out in two or more stages under different reaction conditions. When the multi-stage polymerization is carried out, it is possible to further broaden the molecular weight distribution of the olefin polymer.

30 [0113] Thus obtained olefin polymer may be any one of a homopolymer, a random copolymer, a block copolymer, and the like.

[0114] If the polymerization of an olefin, in particular the polymerization of propylene is carried out by using the catalyst for olefin polymerization, a propylene polymer with high stereoregularity which has a content of the decane-insoluble components of 70% or more, preferably 85% or more, and particularly preferably 90% or more is obtained.

35 [0115] Further, according to the process for producing an olefin polymer of the invention, even when the polymerization is carried out in a small number of stages, for example, one stage, rather than in multi-stages, a polyolefin, in particular polypropylene, having a broad molecular weight distribution can be obtained. The process for producing an olefin polymer of the invention is characterized in that an olefin polymer may be often obtained, which has a higher ratio of the high molecular weight components and a lower ratio of the low molecular weight components (particularly referred to as "Beta" components (sticky components)), as compared with the conventional olefin polymers having the same melt flow rate (MFR) as the present olefin polymer. These characteristics can be confirmed by gel permeation chromatography (GPC) measurement described below, and a polymer having both of a high Mw/Mn value and a high Mz/Mw value can be obtained.

40 [0116] The conventional polypropylene obtained by using a solid titanium catalyst component comprising magnesium, titanium, halogen and an electron donor generally has an Mw/Mn value of 5 or less and an Mz/Mw value of less than 4, which are indicators of the molecular weight distribution as determined by GPC measurement, for example, in the region with an MFR of 1 to 10 g/10 min. However, according to the process for producing an olefin polymer of the invention, an olefin polymer having an Mw/Mn value of 6 to 30, and preferably 7 to 20 can be obtained under the same polymerization conditions as described above. Further, an olefin polymer having an Mz/Mw value of preferably 4 to 15, and more preferably 4.5 to 10 can be obtained. Particularly, according to the process for producing an olefin polymer of the invention, a polymer having a high Mz/Mw value can be often obtained.

50 [0117] It is commonly known to a skilled person in the art that polypropylene having a high Mw/Mn value is excellent in moldability and rigidity. On the other hand, a high Mz/Mw value indicates a high content of high molecular weight components, and thus it is expected that the obtained propylene has high melt tension and excellent moldability.

55 [0118] When the process for producing an olefin polymer of the invention is used, a polymer having a broad molecular weight distribution can be obtained even without the use of multi-stage polymerization, and thus it is possible to make the apparatus for producing a polymer simpler. Further, when the conventional multi-stage polymerization is applied, it is expected that a polymer with more excellent melt tension and moldability can be obtained.

[0119] As other methods for obtaining a polymer having a broad molecular weight distribution, the methods of dissolving

and mixing, or dissolving and kneading the polymers having different molecular weights can be employed, but the polymers obtained by these methods may have insufficient improvement on melt tension or moldability, while involving relatively complicated operations. The reason for this is presumed that the polymers having different molecular weights are basically difficult to be mixed with each other. On the other hand, since the polymers obtained by means of the process for producing an olefin polymer of the invention are mixture of the polymers having extremely broad, different molecular weights in a catalytic level, that is, a nano-level, it is expected that they have high melt tension and excellent moldability.

EXAMPLES

[0120] Hereinbelow, the present invention will be described with reference to Examples, but it should be not construed that the invention is limited to these Examples.

[0121] In the following Examples, the bulk specific gravity, the melt flow rate, the content of the decane-soluble (insoluble) components, the molecular weight distribution, or the like of the propylene polymer were measured by the methods described below.

(1) Bulk specific gravity:

[0122] The bulk specific gravity was measured in accordance with JIS K-6721.

(2) Melt flow rate (MFR):

[0123] The melt flow rate (MFR) was measured in accordance with ASTM D 1238E at a measurement temperature of 230°C in the case of a propylene polymer, and 260°C in the case of a 4-methyl-1-pentene polymer.

(3) Content of decane-soluble (insoluble) components:

[0124] Into the glass container for measurement were introduced about 3 g (measurement was made in the order of 10<sup>-4</sup> g, and the weight was represented by b (g) in the following equation) of a propylene polymer, 500 ml of decane, and a small amount of a heat-resistant stabilizer soluble in decane, and the mixture was stirred with a stirrer while elevating the temperature to 150 °C over 2 hours under a nitrogen atmosphere to dissolve the propylene polymer, maintained at 150°C for 2 hours, and then slowly cooled to 23°C over 8 hours. The solution containing the obtained precipitates of the propylene polymer was filtered under reduced pressure with a glass filter of a 25G-4 specification manufactured by Iwata glass Co., Ltd. 100 ml of the filtrate was taken and dried under reduced pressure to obtain a portion of the decane-soluble components, the weight of which was measured in the order of 10<sup>-4</sup> g (this weight was represented by a (g) in the following equation). After this operation, the amount of the decane-soluble components was determined by the following equation:

$$\text{Content of decane-soluble components} = 100 \times (500 \times a) / (100 \times b)$$

$$\text{Content of decane-insoluble components} = 100 - 100 \times (500 \times a) / (100 \times b)$$

(4) Molecular weight distribution:

[0125] The Mw/Mn value and the Mz/Mw value were calculated by analyzing, using a well-known method, the chromatogram obtained by the measurement under the following conditions. The measurement time per one sample was 60 minutes.

Liquid chromatograph: ALC/GPC 150-C plus type manufactured by Waters Co., Ltd. (Integrated type differential refractometer-detector)

Column: GMH6-HT × 2 and GMH6-HTL × 2 manufactured by Tosoh Corporation connected in series

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Mobile phase medium: o-dichlorobenzene

Flow rate: 1.0 ml/min

Measurement temperature: 140°C

Process for producing calibration curve: Using standard polystyrene sample

5 Concentration of sample: 0.10% (w/w)

Amount of sample solution: 500  $\mu$ l

### (5) Melt tension:

10 **[0126]** Using an apparatus for measurement of melt tension provided with an equipment for measurement of melt tension in a Capirograph "1B" type apparatus manufactured by Toyo Seiki Seisaku-sho, Ltd., the strand of the sample resin, melted for 6 minutes in the cylinder at 230°C (under a nitrogen atmosphere) in the apparatus, was extruded through a nozzle having a length of 8 mm and a diameter of 2.095 mm with a piston. The extrusion speed of the piston was 15 mm/min. This strand was pulled out in the shape of a filament, and wound up using a roller at a predetermined speed  
15 through a pulley provided with the load cell. At this time, the stress force as detected with the load cell was referred to a melt tension.

**[0127]** In addition, as the compound corresponding to the above-described cyclic ester compound (a), a product synthesized by AZUMA-Japan, Inc. was used unless specifically mentioned otherwise. The purities of the isomers of trans- and cis-conformation are both 95% or more unless specifically mentioned otherwise.

20

### Reference Example 1

(Production of solid titanium catalyst component ( $\alpha$ 1))

25 **[0128]** A high speed stirring device having an internal volume of 2 liters (manufactured by Tokushu Kika Kogyo Co., Ltd.) was sufficiently purged with nitrogen, and 700 ml of purified decane, 10 g of commercial available magnesium chloride, 24.2 g of ethanol and 3 g of Leodol (trade name) SP-S20 (sorbitan distearate, manufactured by Kao Corporation) were charged therein. While stirring this suspension, the temperature of the system was elevated and the suspension was stirred at 120°C and 800 rpm for 30 minutes. Then, this suspension was transferred to a 2-liter glass flask (equipped  
30 with a stirrer) which was previously charged with 1 liter of purified decane cooled to -10°C by using a Teflon (registered trade mark) tube having an inner diameter of 5 mm under high speed stirring so as not to generate the precipitates. The solid obtained from liquid transferring was filtered and sufficiently washed with purified n-hexane to obtain a solid adduct in which 2.8 mol of ethanol is coordinated to 1 mol of magnesium chloride.

**[0129]** 46.2 mmol of the solid adduct, in terms of magnesium atom, which was suspended in 30 ml of decane, was wholly introduced into 200 ml of titanium tetrachloride which was maintained at -20°C, under stirring. The temperature of the mixture was elevated to 80°C over 5 hours. When the temperature reached 80°C, diisobutyl 4-methyl-cyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer) was added thereto in a proportion of 0.15 mol, based on 1 mol of a magnesium atom in the solid adduct, and then the temperature thereof was elevated to 120°C over 40 minutes. The temperature was maintained at 120°C under stirring for 90 minutes to effect the reaction.

40 **[0130]** After the completion of the reaction for 90 minutes, a solid portion was recovered by hot filtration. This solid portion was resuspended in 200 ml of titanium tetrachloride, and the temperature thereof was elevated to 130°C, and then maintained at that temperature under stirring for 45 minutes to effect reaction. After the completion of the reaction for 45 minutes, a solid portion was recovered again by hot filtration. The recovered solid portion was sufficiently washed with decane and heptane at 100°C until a free titanium compound was no longer detected in the washing solution.

45 **[0131]** Thus, the solid titanium catalyst component ( $\alpha$ 1) which was prepared in the above procedure was stored as a decane slurry. An aliquot portion of the slurry was picked and dried to examine the catalyst composition.

(Polymerization)

50 **[0132]** To a polymerization vessel with an internal volume of 2 liters, 500 g of propylene and 1 NL of hydrogen were added at room temperature, and then 0.5 mmol of triethylaluminum, 0.1 mmol of cyclohexylmethyldimethoxysilane and 0.004 mmol, in terms of titanium atom, of the solid catalyst component ( $\alpha$ 1) as prepared above were added thereto, and the internal temperature of the polymerization vessel was rapidly elevated to 70°C. After polymerization at 70°C for 1 hour, a small amount of methanol was added thereto to stop the reaction, and propylene was purged. The obtained  
55 polymer particles were dried under reduced pressure overnight at 80°C.

**[0133]** The activity of the catalyst, and the MFR, the content of the decane-insoluble components, the bulk specific gravity, and the molecular weight distribution (Mw/Mn, Mz/Mw) of the obtained polymer were shown in Table 1.

Reference Example 2

(Production of solid titanium catalyst component ( $\alpha_2$ ))

5 **[0134]** In the same manner as in Example 1 except that diethyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer) was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha_2$ ) was obtained.

(Polymerization)

10

**[0135]** In the same manner as in Example 1 except that the solid titanium catalyst component (a1) was used instead of the solid titanium catalyst component (a2), the propylene polymerization was carried out. The results were shown in Table 1.

15 Reference Example 3

(Production of solid titanium catalyst component ( $\alpha_3$ ))

20 **[0136]** In the same manner as in Example 1 except that a cis-isomer of diethyl 4-methyl-4-cyclohexene-1,2-dicarboxylate was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha_3$ ) was obtained.

(Polymerization)

25 **[0137]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha_3$ ) was used, the propylene polymerization was carried out. The results were shown in Table 1.

Reference Example 4

30 (Production of solid titanium catalyst component ( $\alpha_4$ ))

**[0138]** In the same manner as in Example 1 except that di-n-octyl 3-methyl-4-cyclohexene-1,2-dicarboxylate (a mixture of a trans-isomer and a cis-isomer) was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha_4$ ) was obtained.

35

(Polymerization)

**[0139]** In the same manner as in Example 1 except that the solid titanium catalyst component (a4) was used, the propylene polymerization was carried out. The results were shown in Table 1.

40

Reference Example 5

(Production of solid titanium catalyst component ( $\alpha_5$ ))

45 **[0140]** In the same manner as in Example 1 except that a mixture of diisobutyl 3-methyl-4-cyclohexene-1,2-dicarboxylate and diisobutyl 4-methyl-4-cyclohexene-1,2-dicarboxylate was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha_5$ ) was obtained.

(Polymerization)

50

**[0141]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha_5$ ) was used, the propylene polymerization was carried out. The results were shown in Table 1.

Reference Example 6

55

(Production of solid titanium catalyst component ( $\alpha_6$ ))

**[0142]** In the same manner as in Example 1 except that di-n-octyl 3-methyl-4-cyclohexene-1,2-dicarboxylate and di-

n-octyl 4-methyl-4-cyclohexene-1,2-dicarboxylate were used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), solid titanium catalyst component ( $\alpha 6$ ) was obtained.

(Polymerization)

5

**[0143]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha 6$ ) was used, the propylene polymerization was carried out. The results were shown in Table 1.

Example 7

10

(Production of solid titanium catalyst component ( $\alpha 7$ ))

**[0144]** In the same manner as in Example 1 except that diisobutyl norbornane-1,2-dicarboxylate was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha 7$ ) was obtained.

15

(Polymerization)

**[0145]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha 7$ ) was used, the propylene polymerization was carried out. The results were shown in Table 1.

20

Example 8

(Production of solid titanium catalyst component ( $\alpha 8$ ))

25

**[0146]** In the same manner as in Example 1 except that diisobutyl 3, 6-diphenylcyclohexane-1,2-dicarboxylate was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha 8$ ) was obtained.

30

(Polymerization)

**[0147]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha 8$ ) was used, the propylene polymerization was carried out. The results were shown in Table 1.

35

Example 9

(Production of solid titanium catalyst component ( $\alpha 9$ ))

**[0148]** In the same manner as in Example 1 except that diisobutyl 3-methylcyclohexane-1,2-dicarboxylate (a cis-isomer) was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha 9$ ) was obtained.

40

(Polymerization)

**[0149]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha 9$ ) was used, the propylene polymerization was carried out. The results were shown in Table 1.

45

Example 10

(Production of solid titanium catalyst component ( $\alpha 10$ ))

50

**[0150]** In the same manner as in Example 1 except that di-n-octyl 3-methylcyclohexane-1,2-dicarboxylate (a cis-isomer) was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha 10$ ) was obtained.

55

(Polymerization)

**[0151]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha 10$ ) was used, the

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propylene polymerization was carried out. The results were shown in Table 1.

### Example 11

5 (Production of solid titanium catalyst component ( $\alpha$ 11))

**[0152]** In the same manner as in Example 1 except that diisobutyl 3,6-dimethylcyclohexane-1,2-dicarboxylate (content of a trans-isomer: 74%) was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha$ 11) was obtained

10

(Polymerization)

**[0153]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha$ 11) was used, the propylene polymerization was carried out. The results were shown in Table 1.

15

### Example 12

(Production of solid titanium catalyst component ( $\alpha$ 12))

20 **[0154]** In the same manner as in Example 1 except that di-n-octyl 3,6-dimethylcyclohexane-1,2-dicarboxylate (a cis-isomer) was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha$ 12) was obtained.

25

(Polymerization)

**[0155]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha$ 12) was used, the propylene polymerization was carried out. The results were shown in Table 1.

### Example 13

30

(Production of solid titanium catalyst component ( $\alpha$ 13))

**[0156]** In the same manner as in Example 1 except that diisobutyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\alpha$ 13) was obtained.

35

(Polymerization)

**[0157]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\alpha$ 13) was used, the propylene polymerization was carried out. The results were shown in Table 1.

40

### Comparative Example 1

(Synthesis of solid titanium catalyst component ( $\beta$ 1))

45

**[0158]** In the same manner as in Example 1 except that diisobutyl phthalate (reagent of special grade, manufactured by Wako Pure Chemicals Co., Ltd.) was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\beta$ 1) was obtained.

50

(Polymerization)

**[0159]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\beta$ 1) was used, the propylene polymerization was carried out. The results were shown in Table 1.

55



## Comparative Example 2

(Synthesis of diethyl 2,3-diisopropylsuccinate)

5 **[0160]** In the same manner as described in the Patent Document 5, diethyl 2,3-diisopropylsuccinate was synthesized.

(Synthesis of solid titanium catalyst component ( $\beta 2$ ))

10 **[0161]** In the same manner as in Example 1 except that diethyl 2,3-diisopropylsuccinate was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\beta 2$ ) was obtained.

(Polymerization)

15 **[0162]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\beta 2$ ) and 1.6 NL of hydrogen were used, the propylene polymerization was carried out. The results were shown in Table 1.

## Comparative Example 3

20 (Production of solid titanium catalyst component ( $\beta 3$ ))

**[0163]** In the same manner as in Example 1 except that a trans-isomer of diisobutyl cyclohexane-1,2-dicarboxylate was used instead of diisobutyl 4-methylcyclohexane-1,2-dicarboxylate (a mixture of a cis-isomer and a trans-isomer), a solid titanium catalyst component ( $\beta 3$ ) was obtained.

25

(Polymerization)

**[0164]** In the same manner as in Example 1 except that the solid titanium catalyst component ( $\beta 3$ ) was used, the propylene polymerization was carried out. The results were shown in Table 1.

30

Table 1

		Activity kg-PP/g- Cat	MFR g/10 min	Content of Decane -insoluble components wt%	Bulk specific Gravity g/ml	Mw/Mn	Mz/Mn
35	Ref. Ex. 1	17.7	11.2	92.8	0.42	11.5	4.8
40	Ref. Ex. 2	18.5	10.1	93.3	0.44	9.6	4.3
45	Ref. Ex. 3	12.1	14.0	92.4	0.42	6.0	5.1
50	Ref. Ex. 4	20.2	7.6	93.9	0.41	9.2	6.9
55	Ref. Ex. 5	7.5	12.0	92.2	0.42	7.4	7.5

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(continued)

		Activity kg-PP/g- Cat	MFR g/10 min	Content of Decane -insoluble components wt%	Bulk specific Gravity g/ml	Mw/Mn	Mz/Mn
5							
10	Ref. Ex. 6	16.4	12.5	91.0	0.41	9.4	4.9
15	Ex. 7	15.0	16.0	93.5	0.50	7.8	4.7
	Ex. 8	19.9	13.5	91.9	0.49	7.8	4.1
20	Ex. 9	16.7	6.6	93.5	0.43	19.5	7.9
	Ex. 10	19.2	4.9	94.2	0.43	19.6	7.1
25	Ex. 11	25.8	2.9	97.6	0.48	18.2	6.9
30	Ex. 12	20.7	11.5	92.9	0.42	13.1	8.3
35	Ex. 13	28.9	2.6	97.7	0.42	15.7	13.6
	Comp. Ex. 1	22.1	5.0	98.5	0.49	4.3	3.0
40	Comp. Ex. 2	39.7	5.6	97.2	0.39	8.6	4.4
	Comp. Ex. 3	29.8	4.6	97.0	0.42	6.9	4.9

45 **[0165]** The results of the measurement of melt tension were shown in Table 2. It can be seen that PP of Comparative Example 2 has a lower melt tension, as compared with that of Example 11. Further, the threads obtained upon measurement of melt tension of the polymers obtained in Comparative Examples 2 and 3 were weak, and thus troubles such as thread breakages or moving away from the pulley easily occurred.

50 Table 2

	Melt tension / g			
	Receiving speed / (m/min)			
	15	25	45	75
55 Example 11	1.1	1.2	1.2	1.3
Comparative Example 2	0.9	0.7	Thread breakage	Thread breakage

(continued)

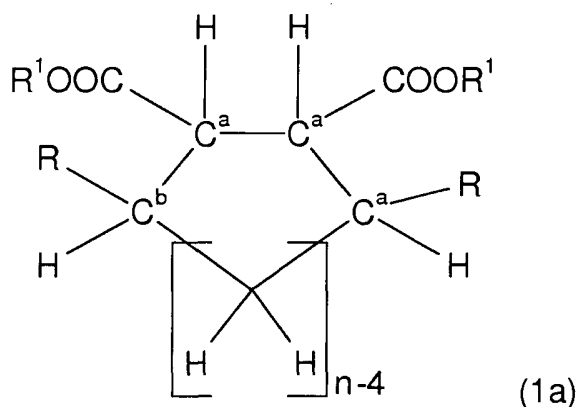
	Melt tension / g			
	Receiving speed / (m/min)			
	15	25	45	75
Comparative Example 3	1.0	1.0	0.9	1.1

**[0166]** It can be seen that polypropylene obtained by using the solid titanium catalyst component, the catalyst for olefin polymerization and the process for producing an olefin polymer of the invention is a polymer having a broad molecular weight distribution. In particular, it is characterized that when comparing the PP's having almost the same MFR values with each other, the Mz/Mw values are high, which shows high contents of the high molecular weight components.

**[0167]** Above all, when using the solid titanium catalyst component comprising a cyclic diester compound having a dicarboxylic acid diester group on the 1-position and the 2-position, and a substituent on the 3-position, a polymer having an extremely high Mw/Mn value is obtained. In particular, it can be seen that the polymer obtained by using the solid titanium catalyst component comprising cyclohexane-1,2-dicarboxylic acid diester (corresponding to the compound of the above-described formula (1a)) having a substituent on the 3-position and the 6-position exhibited extremely high Mw/Mn values and Mz/Mw values, and the activity of the catalyst and the stereoregularity of the obtained polymer are high.

### Claims

1. A solid titanium catalyst component (I), comprising titanium, magnesium, halogen, and a cyclic ester compound (a) represented by the following formula (1a):



wherein n is an integer of 5 to 10;

the bonds between the carbon atoms in the cyclic backbone are all single bonds;

a plurality of R<sup>1</sup>'s are each independently a monovalent hydrocarbon group having 1 to 20 carbon atoms;

a plurality of R's are each independently an atom or group selected from a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a halogen atom, a nitrogen-containing group, an oxygen-containing group, a phosphorus-containing group, a halogen-containing group and a silicon-containing group, and they may be bonded to each other to form a ring, but at least one of R's is not a hydrogen atom; and

in the case where two C<sup>a</sup>'s bonded with COOR<sup>1</sup> are contained in the backbone of the ring, the backbone of the ring has 5 to 10 carbon atoms.

2. A solid titanium catalyst component (I) according to claim 1, wherein in the formula (I), the cyclic backbone has 6 carbon atoms.
3. A solid titanium catalyst component (I) according to claim 1, further comprising an aromatic carboxylic acid ester and/or a compound having two or more ether linkages through a plurality of carbon atoms.
4. A catalyst for olefin polymerization, comprising:

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a solid titanium catalyst component (I) according to any one of claims 1 to 3, and  
an organometallic compound catalyst component (II) containing a metal element selected from Groups I, II and  
XIII of the periodic table.

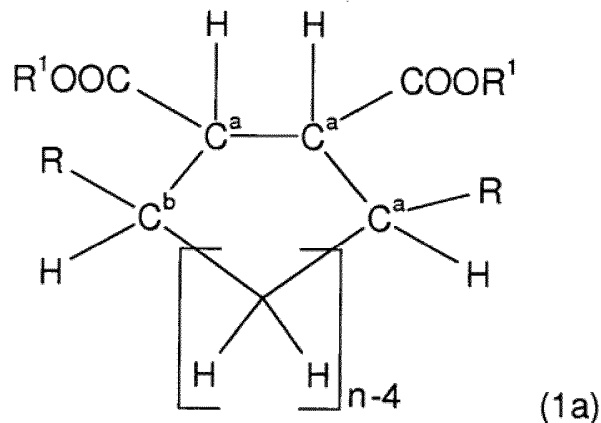
- 5 5. A catalyst for olefin polymerization according to claim 5, further comprising an electron donor (III).
6. A process for producing an olefin polymer, comprising polymerizing an olefin in the presence of the catalyst for olefin  
polymerization according to claim 4 or 5.

10

### Patentansprüche

1. Feste Titankatalysatorkomponente (I), die Titan, Magnesium, Halogen und eine zyklische Esterverbindung (a) der  
folgenden Formel (1a) umfasst:

15



worin n eine ganze Zahl von 5 bis 10 ist;

alle Bindungen zwischen den Kohlenstoffatomen in dem zyklischen Gerüst Einfachbindungen sind;

35

eine Vielzahl von R<sup>1</sup> jeweils unabhängig eine einwertige Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen ist;

eine Vielzahl von R jeweils unabhängig ein Atom oder eine Gruppe, ausgewählt aus einem Wasserstoffatom,  
einer Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen, einem Halogenatom, einer stickstoffhaltigen  
Gruppe, einer sauerstoffhaltigen Gruppe, einer phosphorhaltigen Gruppe, einer halogenhaltigen Gruppe und  
einer siliciumhaltigen Gruppe ist und die R gegebenenfalls miteinander zu einem Ring verbunden sind, wobei  
zumindest eines der R kein Wasserstoffatom ist; und

40

wenn zwei C<sup>a</sup>, die mit COOR<sup>1</sup> verbunden sind, in dem Gerüst des Rings enthalten sind, das Ringgerüst 5 bis  
10 Kohlenstoffatome aufweist.

- 45 2. Feste Titankatalysatorkomponente (I) nach Anspruch 1, worin das zyklische Gerüst in Formel (I) 6 Kohlenstoffatome  
aufweist.
3. Feste Titankatalysatorkomponente (I) nach Anspruch 1, die weiters einen aromatischen Carbonsäureester und/oder  
eine Verbindung mit zwei oder mehr Etherbindungen über eine Vielzahl von Kohlenstoffatomen umfasst.

50

4. Katalysator zur Olefinpolymerisation, der Folgendes umfasst:

eine feste Titankatalysatorkomponente (I) nach einem der Ansprüche 1 bis 3 und

eine organometallische Verbindung als Katalysatorkomponente (II), die ein aus den Gruppen I, II und XIII des  
Periodensystems ausgewähltes Metallelement enthält.

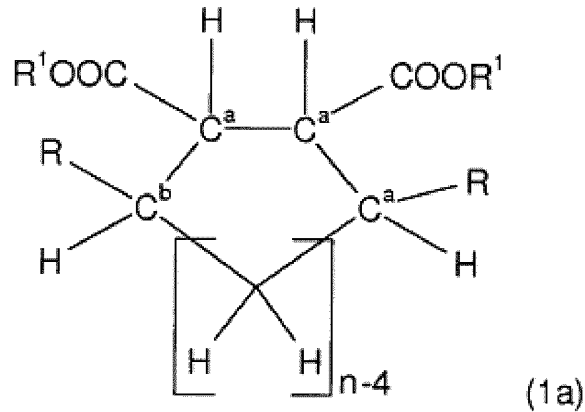
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5. Katalysator zur Olefinpolymerisation nach Anspruch 5, der weiters einen Elektronendonator (III) umfasst.
6. Verfahren zur Herstellung eines Olefinpolymers, das das Polymerisieren eines Olefins in Gegenwart eines Kataly-

sators zur Olefinpolymerisation nach einem der Ansprüche 4 und 5 umfasst.

Revendications

1. Composant catalyseur de titane solide (1), comprenant du titane, du magnésium, de l'halogène et un composé ester cyclique (a) représenté par la formule suivante (1a) :



où n est un entier de 5 à 10 ;

les liaisons entre les atomes de carbone dans le squelette cyclique sont toutes des liaisons simples ;

une pluralité de R<sup>1</sup>s sont chacun indépendamment un groupe d'hydrocarbures monovalents ayant 1 à 20 atomes de carbone ;

une pluralité de R's étant chacun indépendamment un atome ou groupe sélectionné parmi un atome d'hydrogène, un groupe d'hydrocarbures ayant 1 à 20 atomes de carbone, un atome d'halogène, un groupe contenant de l'azote, un groupe contenant de l'oxygène, un groupe contenant du phosphore, un groupe contenant de l'halogène et un groupe contenant du silicium, et ils peuvent être liées les uns aux autres pour former un cycle, mais au moins un des R's n'est pas un atome d'hydrogène ; et

dans le cas où deux C<sup>a</sup>s liés à COOR<sup>1</sup> se trouvent dans le squelette du cycle, le squelette du cycle possède 5 à 10 atomes de carbone.

2. Composant catalyseur de titane solide (1) selon la revendication 1, dans lequel dans la formule (1), le squelette cyclique possède 6 atomes de carbone.
3. Composant catalyseur de titane solide (1) selon la revendication 1, comprenant en outre un ester d'acide carboxylique aromatique et/ou un composé ayant deux ou plusieurs liaisons d'éther par une pluralité d'atomes de carbone.
4. Catalyseur pour une polymérisation d'oléfine, comprenant :
- un composant catalyseur de titane solide (1) selon l'une quelconque des revendications 1 à 3, et
  - un composant catalyseur de composé organométallique (11) contenant un élément de métal sélectionné dans les Groupes I, II et XIII de la table périodique.
5. Catalyseur pour une polymérisation d'oléfine selon la revendication 5, comprenant en outre un donneur d'électrons (111).
6. Procédé pour produire un polymère d'oléfine, comprenant la polymérisation d'une oléfine en présence du catalyseur pour la polymérisation d'oléfine selon la revendication 4 ou 5.

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 57063310 A [0005] [0010]
- JP 5170843 A [0008] [0010]
- JP 3007703 A [0008] [0010]
- WO 01057099 A [0008] [0010]
- WO 0063261 A [0008] [0010]
- WO 0230998 A [0008] [0010]
- JP 2001114811 A [0009] [0010]
- JP 2003040918 A [0009] [0010]
- US 4725656 A [0010]
- JP 2001354714 A [0060]
- EP 585869 A1 [0073] [0076]
- EP 0585869 A [0073]
- WO 2004016662 A [0080]

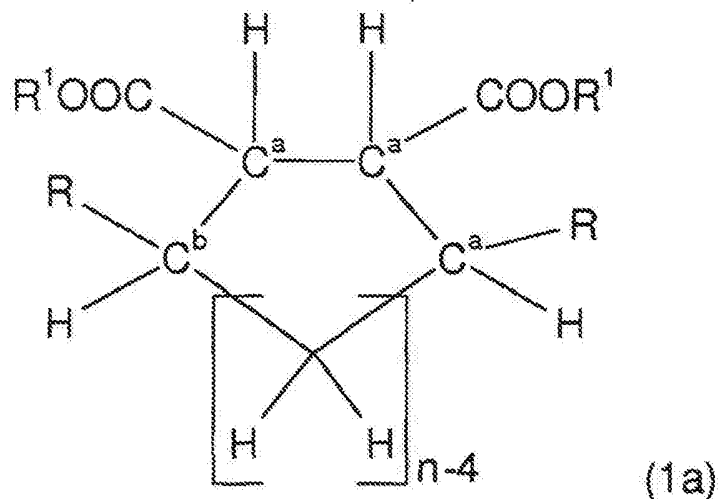
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## SZILÁRD TITÁN-KATALIZÁTOR KOMPONENS, KATALIZÁTOR OLEFIN-POLIMERIZÁCIÓHOZ, ÉS ELJÁRÁS OLEFIN-POLIMER ELŐÁLLÍTÁSÁRA

Szabadalmi igénypontok:

1. Szilárd titánkatalizátor komponens (I), amely tartalmaz titánt, magnéziumot, halogént és gyűrűs észter-vegyületet (a), amely a következő (1a) képlettel jellemezhető:



ahol  $n$  jelentése egész szám, értéke 5 - 10;

a gyűrűs vázban a szénatomok közötti kötések mindegyike egyszeres kötés;

a több  $R^1$  mindegyikének a jelentése egymástól függetlenül egy vegyértékű 1-20 szénatomos szénhidrogéncsoport;

a több  $R$  mindegyikének a jelentését egymástól függetlenül a hidrogénatom, 1-20 szénatomos szénhidrogéncsoport, halogénatom, nitrogéntartalmú csoport, oxigéntartalmú csoport, foszfortartalmú csoport, halogéntartalmú csoport és szilíciumtartalmú csoport által alkotott csoportból választjuk, és ezek kapcsolódhatnak egymáshoz gyűrű képzése közben, de az  $R$ -ek közül legalább egynek a jelentése nem hidrogénatom; és

abban az esetben, ahol a gyűrű vázában két olyan  $C^a$  van, amelyhez  $COOR^1$  csoport kapcsolódik, a gyűrű váza 5-10 szénatomos.

2. Az 1. igénypont szerinti szilárd titánkatalizátor komponens (I), ahol az (I) képletben a gyűrűs váz 6 szénatomos.
3. Az 1. igénypont szerinti szilárd titánkatalizátor komponens (I), amely továbbá tartalmaz aromás karbonsav-észtert és/vagy olyan vegyületet, amely két vagy több éterkötést tartalmaz több szénatomon át.
4. Katalizátor olefin-polimerizációhoz, amely tartalmaz:  
az 1-3. igénypontok bármelyike szerinti szilárd titánkatalizátor komponens (I), és szerves fémvegyület katalizátor komponens (II), amely tartalmaz fémelemet, amelyet a periódusos táblázat I, II és XIII csoportjából választunk.
5. Az 5. igénypont szerinti katalizátor olefin-polimerizációhoz, amely tartalmaz továbbá elektrondonort (III).
6. Eljárás olefin-polimer előállítására, amely során olefint a 4. vagy 5. igénypont szerinti, olefin-polimerizációra alkalmas katalizátor jelenlétében polimerizálunk.