

REPLACED SHEETS

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CATALYST FOR COPOLYMERIZING ETHYLENE WITH α -OLEFIN
 AND PROCESS FOR PRODUCING ETHYLENE- α -OLEFIN COPOLYMER
 USING THE CATALYST

1

The present invention relates to a novel Ziegler catalyst and to a process for producing ethylene- α -olefin copolymers using the catalyst. In more particular, it relates to a catalyst comprising a novel catalyst component and an organoaluminum compound and to a process for producing ethylene- α -olefin copolymers using the catalyst. In still more particular, it relates to a novel catalyst and to a process for producing ethylene- α -olefin copolymers which have a narrow composition distribution, have a high molecular weight, and are excellent in weather resistance, color development, transparency, corrosiveness and mechanical properties by using the catalyst.

Olefin copolymers are in a vast variety of uses, including film, laminates, electric wire covering, injection molded articles, and special molded articles. It is generally known that, to obtain products which are excellent in transparency, impact resistance and anti-blocking property in these uses, polymers which have narrow molecular weight distribution and composition distribution are preferably used. In the case of

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1 copolymers, particularly, as the content of copolymerized
α-olefin increases, the influences of molecular weight
distribution and composition distribution exerted on the
properties of the copolymer become greater. Accordingly,
5 olefin copolymers which have narrow molecular weight
distribution and composition distribution are eagerly
waited for.

Among the methods for producing olefin
copolymers, there are widely known a group of methods
10 which use so-called Ziegler-natta catalysts, which
comprise a compound of a transition metal of the groups
IV to VI of the periodic table and an organometallic
compound of the groups I to III.

As to Ziegler-type solid catalysts, there have
15 been proposed catalysts comprising a transition metal
compound, such as titanium tetrachloride, supported on a
carrier, such as a magnesium compound (see for example Belgian Patent
Application No. 759601, JP-B-47-46269 and JP-B-47-26383),
and solid catalytic systems obtained by reducing
20 a titanium compound with an organomagnesium compound,
which include a solid catalyst component comprising a
Grignard reagent and titanium tetrachloride or an
alkoxy-containing titanium halide (see for example JP-A-46-4391,
JP-B-47-40959 and JP-B-50-30102), and a solid
25 catalyst component obtained by reacting a Grignard
reagent and an alkoxy-containing titanium halide and
treating the reaction product with titanium tetrachloride
(see for example JP-B-57-24361 and JP-A-56-115302). These



1 catalysts, however, all give copolymers which have a wide
composition distribution and are unsatisfactory in
transparency and mechanical properties.

On the other hand, a method is known for
5 obtaining olefin copolymers having narrow molecular
weight distribution and composition distribution which
uses a catalyst formed from a vanadium-containing
catalyst component and an organoaluminum compound
catalyst component. This catalyst, however, though it
10 gives ethylene- α -olefin copolymers having a narrow
composition distribution, has a low polymerization
activity at high temperatures and hence a low produc-
tivity and, further, raises the problems of color
development, low weather resistance, and corrosiveness
15 due to residual vanadium and chlorine, so that the
copolymer must be thoroughly de-ashed to avoid these
problems.

In order to solve such problems, several
methods have been thus far proposed which use a catalytic
20 system comprising a titanium compound or zirconium
compound and an aluminum compound. Recently, in
particular, a method has been proposed which uses a
catalytic system comprising a titanium compound or
zirconium compound and an aluminoxane (JP-T2-1-503788,
25 JP-A-62-121708).

However, when the above-mentioned catalytic
system is used in high temperature solution polymer-
ization, the resulting copolymer has a low molecular

1 weight and hence has properties rather unsatisfactory for
practical use. Further, the catalytic system is not
satisfactory as to the copolymerizability of α -olefins
and hence requires the presence of a larger amount of
5 expensive α -olefin in the polymerization system; this is
economically disadvantageous.

As to the method of polymerizing or copolymer-
izing olefins using a catalytic system comprising a
compound having a titanium-nitrogen bond and an organo-
10 aluminum compound, there have been proposed a method
which uses a catalytic system comprising a solid
component formed by supporting a titanium amide compound
on a magnesium halide and an organoaluminum compound
(EP-0320169, IT-867243), one which uses a
15 catalytic system comprising a diphenylamide compound of
titanium and an organoaluminum compound (EP-0104374,
JP-B-42-11646), one which uses a catalytic system
comprising an titanium amide compound having an aryl
substituent and an organoaluminum compound (JP-B-42-
20 22691) and, further, one which uses a catalytic system
comprising a titanium amide compound having a lower alkyl
group, such as dimethylamidotitanium trichloride, and an
organoaluminum compound [J. of Polym. Sci., Part A-1,
241, 6 (1968)].

25 However, the catalytic systems disclosed in the
above literatures do not give satisfactory results when
used for copolymerization of ethylene with an α -olefin.
That is, the methods disclosed in EP-0320169 and

1 IT-867243 give ethylene- α -olefin copolymers having a
wide composition distribution, while the methods dis-
closed in EP-0104374, JP-B-42-11646, JP-B-42-22691 and J.
of Polym. Sci. Part A-1, 241, 6 (1968) are not satis-
5 factory in the activity and copolymerizability of the
catalyst and the width of composition distribution of the
copolymer obtained.

To solve the problems described above, the
present inventors previously proposed a process for
10 producing, in copolymerization of ethylene with an α -
olefin, a copolymer having a narrow composition
distribution by using a catalytic system comprising a
titanium compound represented by the formula
 $(R^1R^2N)_{4-(m+n)}TiX_mY_n$, wherein R^1 and R^2 are each a
15 saturated hydrocarbon group having 8-30 carbon atoms, X
is a halogen, Y is an alkoxy group, and m and n are
respectively numbers defined by the equations $1 \leq m \leq 3$
and $0 \leq n \leq 2$, provided that $(m+n)$ is defined by the
equation $1 \leq (m+n) \leq 3$, and an organoaluminum compound
20 (JP-A-2-77412).

The above process, however, is not fully satis-
factory in the activity of the catalyst, though it gives
copolymers having substantially improved composition
distribution.

25

In view of the above situation, the object of
the present invention is to provide a novel catalytic



1 system and to provide a process for producing ethylene-
α-olefin copolymers by using the catalytic system with a
high yield of polymer per unit weight of transition metal
which copolymers have a narrow composition distribution
5 and a high molecular weight and are excellent in weather
resistance, color development, transparency, corrosive-
ness, and mechanical properties.

These objects have been achieved by
providing a catalyst for copolymerizing ethylene with
10 an α-olefin which comprises the reaction product (A) of a
titanium compound (A1) having at least one titanium-
nitrogen bond with an organometallic compound (A2) having
at least one element selected from the groups IA, IIA,
IIB, IIIA and IVA of the periodic table and an organo-
15 aluminum compound (B), and a process for producing
ethylene-α-olefin copolymers which uses the catalyst.

Fig. 1 is a diagram showing the melting
behavior of the copolymer obtained in Example 1
20 determined with a differential scanning calorimeter
(hereinafter abbreviated as DSC).

Fig. 2 is a diagram showing the melting
behavior of the copolymer obtained in Example 3
determined with a DSC.

25 Fig. 3 is a diagram showing the melting
behavior of the copolymer obtained in Comparative Example
1 determined with a DSC.



1 Fig. 4 is a diagram showing the melting
behavior of the copolymer obtained in Example 7 deter-
mined with a DSC.

5 Fig. 5 is a diagram showing the melting
behavior of the copolymer obtained in Example 8 deter-
mined with a DSC.

Fig. 6 is a diagram showing the melting
behavior of the copolymer obtained in Example 9 deter-
mined with a DSC.

10 Fig. 7 is a diagram showing the melting
behavior of the copolymer obtained in Example 10 deter-
mined with a DSC.

Fig. 8 is a diagram showing the melting
behavior of the copolymer obtained in Comparative Example
15 4 determined with a DSC.

Fig. 9 is a flow chart to help understanding
the present invention. The flow chart merely represents
a typical example of the embodiments of the present
invention, and the present invention is in no way limited
20 thereto.

The present invention will now be described in
detail below.

The titanium compound (Al) used in the present
25 invention is a compound which has at least one titanium-
nitrogen bond. It may be, for example, a titanium
compound represented by the formula $(R^1R^2N)_{4-(m+n)}TiX_mY_n$,



1 wherein R^1 and R^2 are each a hydrocarbon group having 1-
30 carbon atoms and may be the same or different, X is a
halogen, Y is an alkoxy group, m is a number defined by
the equation $0 \leq m \leq 3$, and n is a number defined by
5 the equation $0 \leq n \leq 3$, provided that (m+n) is defined
by the equation $0 \leq (m+n) \leq 3$.

The halogen denoted by X in the above formula
may be chlorine, bromine, or iodine, but is preferably
chlorine from the viewpoint of catalytic activity. The
10 group Y in the formula may be, for example, an alkoxy
group having 1-20 carbon atoms, such as methoxy, ethoxy,
propoxy, butoxy, or 2-ethylhexyloxy, but it is not
particularly limited from the viewpoint of the property
of the catalyst obtained.

15 When (m+n) in the formula is greater than 3,
free $TiCl_4$ comes to exist. This unfavorably results in a
wide composition distribution of the copolymer obtained.

Specific examples of such titanium compounds
include dimethylaminotitanium trichloride, bis(dimethyl-
20 amino)titanium dichloride, tris(dimethylamino)titanium
chloride, tetrakis(dimethylamino)titanium, diethylamino-
titanium trichloride, bis(diethylamino)titanium
dichloride, tris(diethylamino)titanium chloride,
tetrakis(diethylamino)titanium, diisopropylaminotitanium
25 trichloride, bis(diisopropylamino)titanium dichloride,
tris(diisopropylamino)titanium chloride, tetrakis(diiso-
propylamino)titanium, dipropylaminotitanium trichloride,
bis(dipropylamino)titanium dichloride, tris(dipropyl-

- 1 amino)titanium chloride, tetrakis(dipropylamino)titanium,
diisobutylaminotitanium trichloride, bis(diisobutyl-
amino)titanium dichloride, tris(diisobutylamino)titanium
chloride, tetrakis(diisobutylamino)titanium, di-tert-
5 butylaminotitanium trichloride, bis(di-tert-butylamino)-
titanium dichloride, tris(di-tert-butylamino)titanium
chloride, tetrakis(di-tert-butylamino)titanium,
dibutylaminotitanium trichloride, bis(dibutylamino)-
titanium dichloride, tris(dibutylamino)titanium
10 chloride, tetrakis(dibutylamino)titanium, dihexylamino-
titanium trichloride, bis(dihexylamino)titanium
dichloride, tris(dihexylamino)titanium chloride,
tetrakis(dihexylamino)titanium, dioctylaminotitanium
trichloride, bis(dioctylamino)titanium dichloride,
15 tris(dioctylamino)titanium chloride, tetrakis(dioctyl-
amino)titanium, didecylaminotitanium trichloride,
bis(didecylamino)titanium dichloride, tris(didecylamino)-
titanium chloride, tetrakis(didecylamino)titanium,
dioctadecylaminotitanium trichloride, bis(dioctadecyl-
20 amino)titanium dichloride, tris(dioctadecylamino)titanium
chloride, tetrakis(dioctadecylamino)titanium, diphenyl-
aminotitanium trichloride, bis(diphenylamino)titanium
dichloride, tris(diphenylamino)titanium chloride,
tetrakis(diphenylamino)titanium, ethoxy(dimethyl-
25 amino)titanium dichloride, ethoxy(diethylamino)titanium
dichloride, ethoxy(dipropylamino)titanium dichloride,
ethoxy(diisopropylamino)titanium dichloride, ethoxy-
(diisobutylamino)titanium dichloride, ethoxy(di-tert-

- 1 butylamino)titanium dichloride, ethoxy(dibutylamino)-
titanium dichloride, ethoxy(dihexylamino)titanium
dichloride, ethoxy(dioctylamino)titanium dichloride,
ethoxy(diphenylamino)titanium dichloride, propoxy(di-
5 methylamino)titanium dichloride, propoxy(diethylamino)-
titanium dichloride, propoxy(dipropylamino)titanium
dichloride, propoxy(diisopropylamino)titanium dichloride,
propoxy(diisobutylamino)titanium dichloride, propoxy(di-
tert-butylamino)titanium dichloride, propoxy(dibutyl-
10 amino)titanium dichloride, propoxy(dihexylamino)titanium
dichloride, propoxy(dioctylamino)titanium dichloride,
propoxy(diphenylamino)titanium dichloride, butoxy-
(dimethylamino)titanium dichloride, butoxy(diethylamino)-
titanium dichloride, butoxy(dipropylamino)titanium
15 dichloride, butoxy(diisopropylamino)titanium dichloride,
butoxy(diisobutylamino)titanium dichloride, butoxy(di-
tert-butylamino)titanium dichloride, butoxy(dibutyl-
amino)titanium dichloride, butoxy(dihexylamino)titanium
dichloride, butoxy(dioctylamino)titanium dichloride,
20 butoxy(diphenylamino)titanium dichloride, hexyloxy-
(dioctylamino) titanium dichloride, 2-ethylhexyloxy-
(dioctylamino)titanium dichloride, decyloxy(dioctyl-
amino)titanium dichloride, ethoxy(didecylamino)titanium
dichloride, hexyloxy(didecylamino)titanium dichloride,
25 2-ethylhexyloxy(didecylamino)titanium dichloride,
decyloxy(didecylamino)titanium dichloride,
ethoxy(dioctadecylamino)titanium dichloride, 2-
ethylhexyloxy(dioctadecylamino)titanium dichloride,

- 1 decyloxy(dioctadecylamino)titanium dichloride
hexyloxybis(dioctylamino)titanium chloride, 2-
ethylhexyloxy bis(dioctylamino)titanium chloride,
decyloxybis(dioctylamino)titanium chloride,
- 5 hexyloxybis(didecylamino)titanium chloride, 2-
ethylhexyloxybis(didecylamino)titanium chloride,
decyloxybis(didecylamino)titanium chloride,
hexyloxybis(dioctadecylamino)titanium chloride, 2-
ethylhexyloxybis(dioctadecylamino)titanium chloride,
- 10 decyloxybis(dioctadecylamino)titanium chloride,
methoxytris(dimethylamino)titanium, ethoxytris-
(dimethylamino)titanium, butoxytris(dimethylamino)-
titanium, hexyloxytris(dimethylamino)titanium, 2-
ethylhexyloxytris(di-methylamino)titanium,
- 15 decyloxytris(dimethylamino)titanium, methoxytris-
(diethylamino)titanium, ethoxytris(diethylamino)titanium,
butoxytris(diethylamino)titanium, hexyloxytris(diethyl-
amino)titanium, 2-ethylhexyloxytris(diethylamino)-
titanium, decyloxytris(diethylamino)titanium, methoxy-
- 20 tris(dipropylamino)titanium, ethoxytris(dipropyl-
amino)titanium, butoxytris(dipropylamino)titanium,
hexyloxytris(dipropylamino)titanium, 2-ethylhexyloxytris-
(dipropylamino)titanium, decyloxytris(dipropylamino)-
titanium, methoxytris(dibutylamino)titanium, ethoxytris-
- 25 (dibutylamino)titanium, butoxytris(dibutylamino)titanium,
hexyloxytris(dibutylamino)titanium, 2-ethylhexyloxy-
tris(dibutylamino)titanium, decyloxytris(dibutylamino)-
titanium, methoxytris(dihexylamino)titanium,

- 1 ethoxytris(dihexylamino)titanium, butoxytris(dihexyl-
amino)titanium, hexyloxytris(dihexylamino)titanium, 2-
ethylhexyloxytris(dihexylamino)titanium, decyloxytris-
(dihexylamino)titanium, methoxytris(diphenylamino)-
5 titanium, ethoxytris(diphenylamino)titanium,
butoxytris(diphenylamino)titanium, hexyloxytris(diphenyl-
amino)titanium, 2-ethylhexyloxytris(diphenylamino)-
titanium, decyloxytris(diphenylamino)titanium,
methoxytris(dioctylamino)titanium, ethoxytris(dioctyl-
10 amino)titanium, butoxytris(dioctylamino)titanium,
hexyloxytris(dioctylamino)titanium, 2-ethylhexyloxy-
tris(dioctylamino)titanium, decyloxytris(dioctylamino)-
titanium, methoxytris(didecylamino)titanium,
ethoxytris(didecylamino)titanium, butoxytris(didecyl-
15 amino)titanium, hexyloxytris(didecylamino)titanium, 2-
ethylhexyloxytris(didecylamino)titanium, decyloxytris-
(didecylamino)titanium, methoxytris(dioctadecylamino)-
titanium, ethoxytris(dioctadecylamino)titanium,
butoxytris(dioctadecylamino)titanium, hexyloxytris-
20 (dioctadecylamino)titanium, 2-ethylhexyloxytris-
(dioctadecylamino)titanium, and decyloxytris-
(dioctadecylamino)titanium.

Among such titanium compounds, those wherein R^1
and R^2 are each an aliphatic hydrocarbon group are
25 preferred because they yield copolymers having a narrow
composition distribution. Specific examples of such
compounds include dimethylaminotitanium trichloride,
bis(dimethylamino)titanium dichloride, tris(dimethyl-

- 1 amino)titanium chloride, tetrakis(dimethylamino)titanium,
diethylaminotitanium trichloride, bis(diethylamino)-
titanium dichloride, tris(diethylamino)titanium chloride,
tetrakis(diethylamino)titanium, diisopropylaminotitanium
5 trichloride, bis(diisopropylamino)titanium dichloride,
tris(diisopropylamino)titanium chloride, tetrakis(diiso-
propylamino)titanium, dipropylaminotitanium trichloride,
bis(dipropylamino)titanium dichloride, tris(dipropyl-
amino)titanium chloride, tetrakis(dipropylamino)titanium,
10 diisobutylaminotitanium trichloride, bis(diisobutyl-
amino)titanium dichloride, tris(diisobutylamino)titanium
chloride, tetrakis(diisobutylamino)titanium, di-tert-
butylaminotitanium trichloride, bis(di-tert-butylamino)-
titanium dichloride, tris(di-tert-butylamino)titanium
15 chloride, tetrakis(di-tert-butylamino)titanium,
dibutylaminotitanium trichloride, bis(dibutylamino)-
titanium dichloride, tris(dibutylamino)titanium chloride,
tetrakis(dibutylamino)titanium, dihexylaminotitanium
trichloride, bis(dihexylamino)titanium dichloride,
20 tris(dihexylamino)titanium chloride, tetrakis-
(dihexylamino)titanium, dioctylaminotitanium trichloride,
bis(dioctylamino)titanium dichloride, tris(dioctyl-
amino)titanium chloride, tetrakis(dioctylamino)titanium,
didecylaminotitanium trichloride, bis(didecylamino)-
25 titanium dichloride, tris(didecylamino)titanium
chloride, tetrakis(didecylamino)titanium, dioctadecyl-
aminotitanium trichloride, bis(dioctadecylamino)titanium
dichloride, tris(dioctadecylamino)titanium chloride,



- 1 tetrakis(dioctadecylamino)titanium, ethoxy(dimethyl-
amino)titanium dichloride, ethoxy(diethylamino)titanium
dichloride, ethoxy(dipropylamino)titanium dichloride,
ethoxy(diisopropylamino)titanium dichloride, ethoxy-
5 (diisobutylamino)titanium dichloride, ethoxy(di-tert-
butylamino)titanium dichloride, ethoxy(dibutylamino)-
titanium dichloride, ethoxy(dihexylamino)titanium
dichloride, ethoxy(dioctylamino)titanium dichloride,
propoxy(dimethylamino)titanium dichloride, propoxy-
10 (diethylamino)titanium dichloride, propoxy(dipropyl-
amino)titanium dichloride, propoxy(diisopropylamino)-
titanium dichloride, propoxy(diisobutylamino)titanium
dichloride, propoxy(di-tert-butylamino)titanium
dichloride, propoxy(dibutylamino)titanium dichloride,
15 propoxy(dihexylamino)titanium dichloride, propoxy-
(dioctylamino)titanium dichloride, butoxy(dimethyl-
amino)titanium dichloride, butoxy(diethylamino)titanium
dichloride, butoxy(dipropylamino)titanium dichloride,
butoxy(diisopropylamino)titanium dichloride, butoxy-
20 (diisobutylamino)titanium dichloride, butoxy(di-tert-
butylamino)titanium dichloride, butoxy(dibutylamino)-
titanium dichloride, butoxy(dihexylamino)titanium
dichloride, butoxy(dioctylamino)titanium dichloride,
hexyloxy(dioctylamino)titanium dichloride, 2-
25 ethylhexyloxy(dioctylamino)titanium dichloride,
decyloxy(dioctylamino)titanium dichloride, ethoxy-
(didecylamino)titanium dichloride, hexyloxy-
(didecylamino)titanium dichloride, 2-ethylhexyloxy-



- 1 (didecylamino)titanium dichloride, decyloxy(didecyl-
amino)titanium dichloride, ethoxy(dioctadecylamino)-
titanium dichloride, 2-ethylhexyloxy(dioctadecyl-
amino)titanium dichloride, decyloxy(dioctadecylamino)-
5 titanium dichloride, hexyloxybis(dioctylamino)titanium
chloride, 2-ethylhexyloxybis(dioctaylamino)titanium
cyloride, decyloxybis(dioctylamino)titanium chloride,
hexyloxybis(didecylamino)titanium chloride, 2-
ethylhexyloxybis(didecylamino)titanium chloride,
10 decyloxybis(didecylamino)titanium chloride,
hexyloxybis(dioctadecylamino)titanium chloride, 2-
ethylhexyloxybis(dioctadecylamino)titanium chloride,
decyloxybis(dioctadecylamino)titanium chloride,
methoxytris(dimethylamino)titanium, ethoxytris-
15 (dimethylamino)titanium, butoxytris(dimethylamino)-
titanium, hexyloxytris(dimethylamino)titanium, 2-
ethylhexyloxytris(dimethylamino)titanium, decyloxytris-
(dimethylamino)titanium, methoxytris(diethylamino)-
titanium, ethoxytris(diethylamino)titanium,
20 butoxytris(diethylamino)titanium, hexyloxytris-
(diethylamino)titanium, 2-ethylhexyloxytris(diethyl-
amino)titanium, decyloxytris(diethylamino)titanium,
methoxytris(dipropylamino)titanium, ethoxytris-
(dipropylamino)titanium, butoxytris(dipropylamino)-
25 titanium, hexyloxytris(dipropylamino)titanium, 2-
ethylhexyloxytris(dipropylamino)titanium, decyloxytris-
(dipropylamino)titanium, methoxytris(dibutylamino)-
titanium, ethoxytris(dibutylamino)titnaum,



1 butoxytris(dibutylamino)titanium, hexyloxytris(dibutyl-
amino)titanium, 2-ethylhexyloxytris(di-butylamino)-
titanium, decyloxytris(dibutylamino)titanium,
methoxytris(dihexylamino)titanium, ethoxytris(dihexyl-
5 amino)titanium, butoxytris(dihexylamino)titanium,
hexyloxytris(dihexylamino)titanium, 2-ethylhexyloxy-
tris(dihexylamino)titanium, decyloxytris(dihexylamino)-
titanium, methoxytris(dioctylamino)titanium,
ethoxytris(dioctylamino)titanium, butoxytris(dioctyl-
10 amino)titanium, hexyloxytris(dioctylamino)titanium, 2-
ethylhexyloxytris(dioctylamino)titanium, decyloxytris-
(dioctylamino)titanium, methoxytris(didecylamino)-
titnaium, ethoxytris(didecylamino)titanium, butoxytris-
(didecylamino)titanium, hexyloxytris(didecylamino)-
15 titanium, 2-ethylhexyloxytris(didecylamino)titanium,
decyloxytris(didecylamino)titnaium, methoxytris-
(dioctadecylamino)titnaium, ethoxytris(dioctadecyl-
amino)titanium, butoxytris(dioctadecylamino)titnaium,
hexyloxytris(dioctadecylamino)titanium, 2-ethylhexyloxy-
20 tris(dioctadecylamino)titanium, and decyloxytris-
(dioctadecylamino)titanium.

Among such titanium compounds, when R^1 and R^2
are each an aliphatic hydrocarbon group, particularly
those wherein the number of carbon atoms is 8-30 are
25 preferred. Further, even when the number of carbon atoms
is less than 8, those compounds wherein m is 0 or 2 are
more preferred because they give copolymers having a
narrower composition distribution. Specific examples of



- 1 such compounds include bis(dimethylamino)titanium
dichloride, tetrakis(dimethylamino)titanium,
bis(diethylamino)titanium dichloride, tetrakis-
(diethylamino)titanium, bis(diisopropylamino)titanium
5 dichloride, tetrakis(diisopropylamino)titanium,
bis(dipropylamino)titanium dichloride, tetrakis(dipropyl-
amino)titanium, bis(diisobutylamino)titanium dichloride,
tetrakis(diisobutylamino)titanium, bis(di-tert-
butylamino)titanium dichloride, tetrakis(di-tert-
10 butylamino)titanium, bis(dibutylamino)titanium
dichloride, tetrakis(dibutylamino)titanium, bis(dihexyl-
amino)titanium dichloride, tetrakis(dihexylamino)-
titanium, dioctylaminotitanium trichloride, bis-
(dioctylamino)titanium dichloride, tris(dioctyl-
15 amino)titanium chloride, tetrakis(dioctylamino)titanium,
didecylaminotitanium trichloride, bis(didecylamino)-
titanium dichloride, tris(didecylamino)titanium chloride,
tetrakis(didecylamino)titanium, dioctadecylaminotitanium
trichloride, bis(dioctadecylamino)titanium dichloride,
20 tris(dioctadecylamino)titanium chloride, tetrakis-
(dioctadecylamino)titanium, ethoxy(dimethylamino)titanium
dichloride, ethoxy(diethylamino)titanium dichloride,
ethoxy(dipropylamino)titanium dichloride, ethoxy(diiso-
propylamino)titanium dichloride, ethoxy(diisobutylamino)-
25 titanium dichloride, ethoxy(di-tert-butylamino)titanium
dichloride, ethoxy(dibutylamino)titanium dichloride,
ethoxy(dihexylamino)titanium dichloride, ethoxy-
(dioctylamino)titanium dichloride, propoxy(dimethyl-



- 1 amino)titanium dichloride, propoxy(diethylamino)titanium
dichloride, propoxy(dipropylamino)titanium dichloride,
propoxy(diisopropylamino)titanium dichloride, propoxy-
(diisobutylamino)titanium dichloride, propoxy(di-tert-
5 butylamino)titanium dichloride, propoxy(dibutylamino)-
titanium dichloride, propoxy(dihexylamino)titanim
dichloride, propoxy(dioctylamino)titanium dichloride,
butoxy(dimethylamino)titanium dichloride, butoxy-
(diethylamino)titanium dichloride, butoxy(dipropyl-
10 amino)titanium dichloride, butoxy(diisopropylamino)-
titanium dichloride, butoxy(diisobutylamino)titanium
dichloride, butoxy(di-tert-butylamino)titanium
dichloride, butoxy(dibutylamino)titanium dichloride,
butoxy(dihexylamino)titanium dichloride, butoxy-
15 (dioctylamino)titanium dichloride, hexyloxy(dioctyl-
amino)titanium dichloride, 2-ethylhexyloxy(dioctyl-
amino)titanium dichloride, decyloxy(dioctylamino)titanium
dichloride, ethoxy(didecylamino)titanium dichloride,
hexyloxy(didecylamino)titanium dichloride, 2-
20 ethylhexyloxy(didecylamino)titanium dichloride,
decyloxy(didecylamino)titanium dichloride, ethoxy-
(dioctadecylamino)titanium dichloride, 2-ethylhexyloxy-
(dioctadecylamino)titnaium dichloride, decyloxy(diocta-
decylamino)titanium dichloride, hexyloxybis(dioctyl-
25 amino)titanium chloride, 2-ethylhexyloxybis(dioctyl-
amino)titanium chloride, decyloxybis(dioctyl-
amino)titanium chloride, hexyloxybis(didecylamino)-
titanium chloride, 2-ethylhexyloxybis(didecylamino)-



- 1 titanium chloride, decyloxybis(didecylamino)titanium
chloride, hexyloxybis(dioctadecylamino)titanium chloride,
2-ethylhexyloxybis(dioctadecylamino)titanium chloride,
decyloxybis(dioctadecylamino)titanium chloride,
- 5 methoxytris(dimethylamino)titanium, ethoxytris(dimethyl-
amino)titanium, butoxytris(dimethylamino)titanium,
hexyloxytris(dimethylamino)titanium, 2-ethylhexyloxy-
tris(dimethylamino)titanium, decyloxytris(dimethylamino)-
titanium, methoxytris(diethylamino)titanium, ethoxytris-
- 10 (diethylamino)titanium, butoxytris(diethylamino)titanium,
hexyloxytris(diethylamino)titanium, 2-ethylhexyloxytris-
(diethylamino)titanium, decyloxytris(diethylamino)-
titanium, methoxytris(dipropylamino)titanium,
ethoxytris(dipropylamino)titanium, butoxytris(dipropyl-
- 15 amino)titanium, hexyloxytris(dipropylamino)titanium, 2-
ethylhexyloxytris(dipropylamino)titanium, decyloxytris-
(dipropylamino)titanium, methoxytris(dibutylamino)-
titanium, ethoxytris(dibutylamino)titanium, butoxytris-
(dibutylamino)titanium, hexyloxytris(dibutylamino)-
- 20 titanium, 2-ethylhexyloxytris(dibutylamino)titanium,
decyloxytris(dibutylamino)titanium, methoxytris(dihexyl-
amino)titanium, ethoxytris(dihexylamino)titanium,
butoxytris(dihexylamino)titanium, hexyloxytris(dihexyl-
amino)titanium, 2-ethylhexyloxytris(dihexylamino)-
- 25 titanium, decyloxytris(dihexylamino)titanium,
methoxytris(dioctylamino)titanium, ethoxytris(dioctyl-
amino)titanium, butoxytris(dioctylamino)titanium,
hexyloxytris(dioctylamino)titanium, 2-ethylhexyloxytris-

1 (dioctylamino)titanium, decyloxytris(dioctylamino)-
titanium, methoxytris(didecylamino)titanium, ethoxy-
tris(didecylamino)titanium, butoxytris(didecylamino)-
titanium, hexyloxytris(didecylamino)titanium, 2-
5 ethylhexyloxytris(didecylamino)titanium, decyloxytris-
(didecylamino)titanium, methoxytris(dioctadecylamino)-
titanium, ethoxytris(dioctadecylamino)titanium,
butoxytris(dioctadecylamino)titanium, hexyloxytris-
(dioctadecylamino)titanium, 2-ethylhexyloxytris-
10 (dioctadecylamino)titanium, and decyloxytris-
(dioctadecylamino)titanium.

Among such titanium compounds, those wherein m
in the formula is 1 are particularly preferred because
they give the highest catalytic activity. Examples of
15 such compounds include tris(dioctylamino)titanium
chloride, tris(didecylamino)titanium chloride, tris-
(dioctadecylamino)titanium chloride, hexyloxybis(dioctyl-
amino)titanium chloride, 2-ethylhexyloxybis(dioctyl-
amino)titanium chloride, decyloxybis(dioctylamino)-
20 titanium chloride, hexyloxybis(didecylamino)titanium
chloride, 2-ethylhexyloxybis(didecylamino)titanium
chloride, decyloxybis(didecylamino)titanium chloride,
hexyloxybis(octadecylamino)titanium chloride, 2-
ethylhexyloxybis(octadecylamino)titanium chloride, and
25 decyloxybis(octadecylamino)titanium chloride.

When the organometallic compound (A2) is an
organoaluminum compound, among such titanium compounds
those wherein m in the formula is smaller are

1 more preferred because they yield copolymers having still
narrower composition distribution. Examples of such
compounds include tetrakis(dimethylamino)titanium,
tetrakis(diethylamino)titanium, tetrakis(dipropylamino)-
5 titanium, tetrakis(diisopropylamino)titanium,
tetrakis(diisobutylamino)titanium, tetrakis(di-tert-
butylamino)titanium, tetrakis(dibutylamino)titanium,
tetrakis(dihexylamino)titanium, tetrakis(dioctylamino)-
titanium, tetrakis(didecylamino)titanium, tetrakis-
10 (dioctadecyl)titanium, methoxytris(dimethylamino)-
titanium, ethoxytris(dimethylamino)titanium, butoxytris-
(dimethylamino)titanium, hexyloxytris(dimethylamino)-
titanium, 2-ethylhexyloxytris(dimethylamino)titanium,
decyloxytris(dimethylamino)titanium, methoxytris-
15 (diethylamino)titanium, ethoxytris(diethylamino)titanium,
butoxytris(diethylamino)titanium, hexyloxytris(diethyl-
amino)titanium, 2-ethylhexyloxytris(diethylamino)-
titanium, decyloxytris(diethylamino)titanium, methoxy-
tris(dipropylamino)titanium, ethoxytris(dipropylamino)-
20 titanium, butoxytris(dipropylamino)titanium, hexyloxy-
tris(dipropylamino)titanium, 2-ethylhexyloxytris-
(dipropylamino)titanium, decyloxytris(dipropylamino)-
titanium, methoxytris(dibutylamino)titanium, ethoxytris-
(dibutylamino)titanium, butoxytris(dibutylamino)titanium,
25 hexyloxytris(dibutylamino)titanium, 2-ethylhexyloxytris-
(dibutylamino)titanium, decyloxytris(dibutylamino)-
titanium, methoxytris(dihexylamino)titanium, ethoxytris-
(dihexylamino)titanium, butoxytris(dihexylamino)titanium,

1 hexyloxytris(dihexylamino)titanium, 2-ethylhexyloxytris-
(dihexylamino)titanium, decyloxytris(dihexylamino)-
titanium, methoxytris(dioctylamino)titanium, ethoxytris-
(dioctylamino)titnaum, butoxytris(dioctylamino)titnaum,
5 hexyloxytris(dioctylamino)titnaum, 2-ethylhexyloxytris-
(dioctylamino)titanium, decyloxytris(dioctylamino)-
titanium, methoxytris(didecylamino)titanium, ethoxytris-
(didecylamino)titanium, butoxytris(didecylamino)titanium,
hexyloxytris(didecylamino)titanium, 2-ethylhexyloxy-
10 tris(didecylamino)titanium, decyloxytris(didecylamino)-
titanium, methoxytris(dioctadecylamino)titanium,
ethoxytris(dioctadecylamino)titanium, butoxytris-
(dioctadecylamino)titanium, hexyloxytris(dioctadecyl-
amino)titanium, 2-ethylhexyloxytris(dioctadecyl-
15 amino)titanium, and decyloxytris(dioctadecylamino)-
titanium.

Such titanium compounds (A1) may be synthesized, for example, by using the methods described in JP-B-41-5397; JP-B-42-11646; H. Burger et al., J. of
20 Organomet. Chem., 108 (1976), 69-84; H. Burger et al., J. of Organomet. Chem., 20 (1969), 129-139; and H. Burger, Z. Anorg. Allg. Chem., 365, 243-254 (1991).

The titanium compounds may be synthesized, according to the aforesaid methods, for example, by
25 reacting (i) a secondary amine represented by the formula $R^{11}R^{12}NH$, wherein R^{11} and R^{12} each denote a hydrocarbon group haaving 1-30 carbon atoms and may be the same or different, with (ii) an alkylalkali metal represented by



1 the formula $R^{13}M$, wherein R^{13} denotes a hydrocarbon group
having 1-30 carbon atoms and M denotes an alkali metal
such as Li and K, and then reacting the resulting alkali
metal amide with a titanium tetrahalide represented by
5 the formula TiX_4 , wherein X denotes a halogen, such as
chlorine, bromine, or iodine, preferably chlorine.

In the above synthesis, two or more alkali
metal amides may be used simultaneously in combination.

The organometallic compound (A2) used for the
10 synthesis of the reaction product (A) in the present
invention is an organometallic compound having at least
one element selected from the groups IA, IIA, IIB, IIIA
and IVA of the periodic table. It is preferably an
organometallic compound having at least one element
15 selected from Li, Na, K, Be, Mg, Ca, Zn, Cd, B, Al, Ga,
In and Sn. Such organometallic compound may be, for
example, a known organolithium compound, organosodium
compound, organopotassium compound, organoberyllium
compound, organomagnesium compound, organocalcium
20 compound, organozinc compound, organocadmium compound,
organoboron compound, organoaluminum compound,
organogallium compound, organoindium compound, and
organotin compound. It is preferably an organolithium
compound, organoberyllium compound, organomagnesium
25 compound, organozinc compound, organopotassium compound,
organoaluminum compound or organoindium compound. More
preferably, it is an organomagnesium compound, organo-
lithium compound, or organoaluminum compound.



1 The organomagnesium compound used in the
present invention may be any type of organomagnesium
compound which contains a magnesium-carbon bond.
Examples of the organomagnesium compound (A2) include
5 organomagnesium compounds represented by the formula
 R^3R^4Mg , wherein R^3 and R^4 each denote a hydrocarbon group
having 1-20 carbon atoms, the formula R^5MgZ^1 , wherein R^5
denotes a hydrocarbon group having 1-20 carbon atoms, and
 Z^1 denotes a hydrogen atom or alkoxy group, and the
10 formula R^6MgX , wherein R^6 denotes a hydrocarbon group
having 1-20 carbon atoms and X denotes a halogen. In the
above formulas, R^3 , R^4 , R^5 and R^6 may be the same or
different and each denote an alkyl group, aryl group,
aralkyl group or alkenyl group each having 1-20 carbon
15 atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl,
sec-butyl, tert-butyl, amyl, isoamyl, hexyl, octyl, 2-
ethylhexyl, phenyl, benzyl, vinyl, 1-propenyl and 2-
propenyl.

 Specific examples of the compounds represented
20 by the formula R^3R^4Mg include dimethylmagnesium,
diethylmagnesium, dipropylmagnesium, diisopropyl-
magnesium, dibutylmagnesium, diisobutylmagnesium,
di-sec-butylmagnesium, di-tert-butylmagnesium,
diamylmagnesium, dineopentylmagnesium, dihexylmagnesium,
25 dicyclohexylmagnesium, diphenylmagnesium, dibenzyl-
magnesium, divinylmagnesium, di-2-propenylmagnesium,
di-2-butenylmagnesium, bis(trimethylsilylmethyl)-
magnesium, methylethylmagnesium, methylpropylmagnesium,

- 1 methylisopropylmagnesium, methylbutylmagnesium,
methylisobutylmagnesium, methyl-sec-butylmagnesium,
methyl-tert-butylmagnesium, methylamylmagnesium,
methylneopentylmagnesium, methylhexylmagnesium,
- 5 methylcyclohexylmagnesium, methylphenylmagnesium,
methylbenzylmagnesium, methylvinylmagnesium, methyl-2-
propenylmagnesium, methyl-2-butenylmagnesium, methyl-
(trimethylsilylmethyl)magnesium, ethylpropylmagnesium,
ethylisopropylmagnesium, ethylbutylmagnesium, ethyl-
- 10 isobutylmagnesium, ethyl-sec-butylmagnesium, ethyl-tert-
butylmagnesium, ethylamylmagnesium, ethylneopentyl-
magnesium, ethylhexylmagnesium, ethylcyclohexylmagnesium,
ethylphenylmagnesium, ethylbenzylmagnesium, ethylvinyl-
magnesium, ethyl-2-propenylmagnesium, ethyl-2-
- 15 butenylmagnesium, ethyl(trimethylsilylmethyl)magnesium,
propylisopropylmagnesium, propylbutylmagnesium,
propylisobutylmagnesium, propyl-sec-butylmagnesium,
propyl-tert-butylmagnesium, propylamylmagnesium,
propylneopentylmagnesium, propylhexylmagnesium,
- 20 propylcyclohexylmagnesium, propylphenylmagnesium,
propylbenzylmagnesium, propylvinylmagnesium, propyl-2-
propenylmagnesium, propyl-2-butenylmagnesium, propyl-
(trimethylsilylmethyl)magnesium, isopropylbutylmagnesium,
isopropylisobutylmagnesium, isopropyl-sec-butylmagnesium,
- 25 isopropyl-tert-butylmagnesium, isopropylamylmagnesium,
isopropylneopentylmagnesium, isopropylhexylmagnesium,
isopropylcyclohexylmagnesium, isopropylphenylmagnesium,
isopropylbenzylmagnesium, isopropylvinylmagnesium,

- 1 isopropyl-2-propenylmagnesium, isopropyl-2-butenyl-
magnesium, isopropyl(trimethylsilylmethyl)magnesium,
butylisobutylmagnesium, butyl-sec-butylmagnesium, butyl-
tert-butylmagnesium, butylamylmagnesium, butylneopentyl-
5 magnesium, butylhexylmagnesium, butylcyclohexylmagnesium,
butylphenylmagnesium, butylbenzylmagnesium, butylvinyl-
magnesium, butyl-2-propenylmagnesium, butyl-2-butenyl-
magnesium, butyl(trimethylsilylmethyl)magnesium,
isobutyl-sec-butylmagnesium, isobutyl-tert-butyl-
10 magnesium, isobutylamylmagnesium, isobutylneopentyl-
magnesium, isobutylhexylmagnesium, isobutylcyclohexyl-
magnesium, isobutylphenylmagnesium, isobutylbenzyl-
magnesium, isobutylvinylmagnesium, isobutyl-2-
propenylmagnesium, isobutyl-2-butenylmagnesium,
15 isobutyl(trimethylsilylmethyl)magnesium, sec-butyl-tert-
butylmagnesium, sec-butylamylmagnesium, sec-butylneo-
pentylmagnesium, sec-butylhexylmagnesium, sec-
butylcyclohexylmagnesium, sec-butylphenylmagnesium, sec-
butylbenzylmagnesium, sec-butylvinylmagnesium, sec-butyl-
20 2-propenylmagnesium, sec-butyl-2-butenylmagnesium, sec-
butyl(trimethylsilylmethyl)magnesium, tert-butylamyl-
magnesium, tert-butylneopentylmagnesium, tert-
butylhexylmagnesium, tert-butylcyclohexylmagnesium,
tert-butylphenylmagnesium, tert-butylbenzylmagnesium,
25 tert-butylvinylmagnesium, tert-butyl-2-propenylmagnesium,
tert-butyl-2-butenylmagnesium, tert-butyl(trimethyl-
silylmethyl)magnesium, amylneopentylmagnesium, amylhexyl-
magnesium, amylcyclohexylmagnesium, amylphenylmagnesium,

- 1 amylbenzylmagnesium, amylvinylmagnesium, amyl-2-
propenylmagnesium, amyl-2-butenylmagnesium, amyl-
(trimethylsilylmethyl)magnesium, neopentylhexylmagnesium,
neopentylcyclohexylmagnesium, neopentylphenylmagnesium,
5 neopentylbenzylmagnesium, neopentylvinylmagnesium,
neopentyl-2-propenylmagnesium, neopentyl-2-butenyl-
magnesium, neopentyl(trimethylsilylmethyl)magnesium,
hexylcyclohexylmagnesium, hexylphenylmagnesium,
hexylbenzylmagnesium, hexylvinylmagnesium, hexyl-2-
10 propenylmagnesium, hexyl-2-butenylmagnesium, hexyl-
(trimethylsilylmethyl)magnesium, cyclohexylphenyl-
magnesium, cyclohexylbenzylmagnesium, cyclohexylvinyl-
magnesium, cyclohexyl-2-propenylmagnesium, cyclohexyl-
2-butenylmagnesium, cyclohexyl(trimethylsilylmethyl)-
15 magnesium, phenylbenzylmagnesium, phenylvinylmagnesium,
phenyl-2-propenylmagnesium, phenyl-2-butenylmagnesium,
phenyl(trimethylsilylmethyl)magnesium, benzylvinyl-
magnesium, benzyl-2-propenylmagnesium, benzyl-2-
butenylmagnesium, benzyl(trimethylsilylmethyl)magnesium,
20 vinyl-2-propenylmagnesium, vinyl-2-butenylmagnesium, and
vinyl(trimethylsilylmethyl)magnesium.

Examples of the compounds represented by the
formula R^5MgZ^1 include ethylmagnesium hydride,
propylmagnesium hydride, isopropylmagnesium hydride,
25 butylmagnesium hydride, sec-butylmagnesium hydride,
tert-butylmagnesium hydride, phenylmagnesium hydride,
ethylmagnesium methoxide, ethylmagnesium ethoxide,
ethylmagnesium propoxide, ethylmagnesium butoxide,



- 1 ethylmagnesium phenoxide, propylmagnesium methoxide,
propylmagnesium ethoxide, propylmagnesium propoxide,
propylmagnesium butoxide, propylmagnesium phenoxide,
isopropylmagnesium methoxide, isopropylmagnesium
5 ethoxide, isopropylmagnesium propoxide, isopropyl-
magnesium butoxide, isopropylmagnesium phenoxide,
butylmagnesium methoxide, butylmagnesium ethoxide,
butylmagnesium propoxide, butylmagnesium butoxide,
butylmagnesium phenoxide, sec-butylmagnesium methoxide,
10 sec-butylmagnesium ethoxide, sec-butylmagnesium
propoxide, sec-butylmagnesium butoxide, sec-butyl-
magnesium phenoxide, tert-butylmagnesium methoxide,
tert-butylmagnesium ethoxide, tert-butylmagnesium
propoxide, tert-butylmagnesium butoxide, tert-
15 butylmagnesium phenoxide, phenylmagnesium methoxide,
phenylmagnesium ethoxide, phenylmagnesium propoxide,
phenylmagnesium butoxide and phenylmagnesium phenoxide.

- Examples of the compound represented by the
formula R^6MgX include methylmagnesium chloride,
20 ethylmagnesium chloride, ethylmagnesium bromide,
ethylmagnesium iodide, propylmagnesium chloride,
propylmagnesium bromide, butylmagnesium chloride,
butylmagnesium bromide, sec-butylmagnesium chloride,
sec-butylmagnesium bromide, tert-butylmagnesium chloride,
25 tert-butylmagnesium bromide, amylmagnesium chloride,
isoamylmagnesium chloride, vinylmagnesium bromide,
vinylmagnesium chloride, 1-propenylmagnesium bromide, 1-
propenylmagnesium chloride, 2-propenylmagnesium bromide.



- 1 2-propenylmagnesium chloride, phenylmagnesium chloride, phenylmagnesium bromide, benzylmagnesium chloride, and benzylmagnesium bromide.

From the viewpoint of the composition distribution of the copolymer formed, the organomagnesium compounds are preferably those which are represented by the formula R^3R^4Mg . Among them, those wherein R^3 and R^4 are each an aliphatic hydrocarbon group are more preferred. Specific examples of such organomagnesium compounds include dimethylmagnesium, diethylmagnesium, dipropylmagnesium, diisopropylmagnesium, dibutylmagnesium, diisobutylmagnesium, di-sec-butylmagnesium, di-tert-butylmagnesium, diamylmagnesium, dineopentylmagnesium, dihexylmagnesium, dicyclohexylmagnesium, methylethylmagnesium, methylpropylmagnesium, methylisopropylmagnesium, methylbutylmagnesium, methylisobutylmagnesium, methyl-sec-butylmagnesium, methyl-tert-butylmagnesium, methylamylmagnesium, methylneopentylmagnesium, methylhexylmagnesium, methylcyclohexylmagnesium, ethylpropylmagnesium, ethylisopropylmagnesium, ethylbutylmagnesium, ethylisobutylmagnesium, ethyl-sec-butylmagnesium, ethyl-tert-butylmagnesium, ethylamylmagnesium, ethylneopentylmagnesium, ethylhexylmagnesium, ethylcyclohexylmagnesium, propylisopropylmagnesium, propylbutylmagnesium, propylisobutylmagnesium, propyl-sec-butylmagnesium, propyl-tert-butylmagnesium, propylamylmagnesium, propylneopentylmagnesium, propylhexylmagnesium,



1 propylcyclohexylmagnesium, isopropylbutylmagnesium,
isopropylisobutylmagnesium, isopropyl-sec-butylmagnesium,
isopropyl-tert-butylmagnesium, isopropylamylmagnesium,
isopropylneopentylmagnesium, isopropylhexylmagnesium,
5 isopropylcyclohexylmagnesium, butylisobutylmagnesium,
butyl-sec-butylmagnesium, butyl-tert-butylmagnesium,
butylamylmagnesium, butylneopentylmagnesium, butylhexyl-
magnesium, butylcyclohexylmagnesium, isobutyl-sec-
butylmagnesium, isobutyl-tert-butylmagnesium,
10 isobutylamylmagnesium, isobutylneopentylmagnesium,
isobutylhexylmagnesium, isobutylcyclohexylmagnesium,
sec-butyl-tert-butylmagnesium, sec-butylamylmagnesium,
sec-butylneopentylmagnesium, sec-butylhexylmagnesium,
sec-butylcyclohexylmagnesium, tert-butylamylmagnesium,
15 tert-butylneopentylmagnesium, tert-butylhexylmagnesium,
tert-butylcyclohexylmagnesium, amylneopentylmagnesium,
amylhexylmagnesium, amylcyclohexylmagnesium, neopentyl-
hexylmagnesium, neopentylcyclohexylmagnesium, and
hexylcyclohexylmagnesium.

20 In place of the aforesaid organomagnesium
compounds, hydrocarbon soluble complexes of the
organomagnesium compounds with organometallic compounds
may be used. The organometallic compounds may be, for
example, organic compounds of Li, Be, B, Al or Zn.

25 Further, the present invention is not limited to the
aforesaid compounds.

The organolithium compounds used in the present
invention may be any type of organolithium compounds



- 1 containing a lithium-carbon bond which are represented by the formula R^9Li , wherein R^9 denotes a hydrocarbon group having 1-20 carbon atoms.

Specific examples of such organolithium
5 compounds include methyllithium, ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, isobutyllithium, phenyllithium, aryllithium, cyclohexyllithium, and n-hexyllithium. Preferred among them are methyllithium,
10 ethyllithium, n-propyllithium, n-butyllithium, sec-butyllithium and n-hexyllithium.

The organoberyllium compound may be, for example, diethylberyllium and dipropylberyllium.

The organozinc compound may be, for example,
15 diethylzinc, dibutylzinc and diphenylzinc.

The organocadmium compound may be, for example, diethylcadmium, dibutylcadmium and diphenylcadmium.

The organoboron compound may be, for example, triethylborane, tributylborane, and triphenylborane.

20 The organoaluminum compounds used in the present invention may be those known in the art. Such organoaluminum compounds are, for example, organoaluminum compounds represented by the formula $R^7_aAlZ^2_{3-a}$, or chain-like or cyclic aluminoxanes having a structure
25 represented by the formula $-[Al(R^8)-O]_x-$.

In the above formulas, R^7 and R^8 are each a hydrocarbon group having 1-20 carbon atoms, preferably 1-10 carbon atoms, Z^2 denotes a hydrogen atom and/or an



- 1 alkoxy group, a is a number defined by the equation $0 < a \leq 3$, and ℓ is an integer of 1 or more, preferably 2-30.

Specific examples of the organoaluminum compound represented by the formula $R^7_a AlZ^{2}_{3-a}$ include

5 trialkylaluminums, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, and tridecylaluminum, dialkylaluminum hydrides, such as dimethylaluminum

10 hydride, diethylaluminum hydride, dipropylaluminum hydride, diisobutylaluminum hydride, dihexylaluminum hydride, dioctylaluminum hydride, and didecylaluminum hydride; alkoxyalkylaluminum hydrides, such as

methoxymethylaluminum hydride, methoxyethylaluminum hydride, methoxyisobutylaluminum hydride, ethoxyhexyl-

15 aluminum hydride, ethoxyoctylaluminum hydride, and ethoxydecylaluminum hydride; and alkylaluminum alkoxides, such as dimethylaluminum methoxide, methylaluminum dimethoxide, diethylaluminum methoxide, ethylaluminum dimethoxide, diisobutylaluminum methoxide, isobutyl-

20 aluminum dimethoxide, dihexylaluminum methoxide, hexylaluminum dimethoxide, dimethylaluminum ethoxide, methylaluminum diethoxide, diethylaluminum ethoxide, ethylaluminum diethoxide, diisobutylaluminum ethoxide, and isobutylaluminum diethoxide.

- 25 Among these compounds, preferred from the viewpoint of catalytic activity are trialkylaluminums, which are compounds of the above formula wherein a is 3, for example, trimethylaluminum, triethylaluminum,



1 tripropylaluminum, triisobutylaluminum, trihexylaluminum,
trioctylaluminum, and tridecylaluminum. However, the
present invention is not limited to the above compounds.

Specific examples of aluminoxanes represented
5 by the formula $-\text{[Al(R}^8\text{)-O]}_n-$ include tetramethyl-
dialuminoxane, tetraethyldialuminoxane, tetrabutyl-
dialuminoxane, tetrahexyldialuminoxane, methyl-
aluminoxane, ethylaluminoxane, butylaluminoxane, and
hexylaluminoxane. The present invention, however, is not
10 limited to the above compounds.

The organogallium compounds may be, for
example, diethylgallium, dibutylgallium, and diphenyl
gallium.

The organoindium compounds may be, for example,
15 diethylindium, dibutylindium, and diphenylindium.

The organotin compounds may be, for example,
tetraethyltin, tetrabutyltin, and tetraphenyltin.

The organoaluminum compounds (B) used as one
component of the catalyst in the present invention may be
20 those known in the art. The organoaluminum compounds (B)
may be, for example, organoaluminum compounds (B1)
represented by the formula $\text{R}^{10}_a\text{AlZ}^3_{3-a}$, and chain-like or
cyclic aluminoxanes (B2) having the structure shown by
the formula $-\text{[A}_\ell(\text{R}^{11})\text{-O]}_n-$. Preferred among the
25 organoaluminum compounds (B) are organoaluminum compounds
(B1) represented by the formula $\text{R}^{10}_a\text{AlZ}^3_{3-a}$. In the
above formulas, R^{10} and R^{11} are each a hydrocarbon group
having 1-20 carbon atoms, preferably 1-10 carbon atoms,



- 1 z^3 denotes a hydrogen atom and/or an alkoxy group, a is a number defined by the equation $0 < a \leq 3$, and l is an integer of 1 or more, preferably 2-30.

- Specific examples of the organoaluminum
5 compounds (B1) represented by the formula $R^{10}_a AlZ^3_{3-a}$ include trialkylaluminums, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, and tridecylaluminum, dialkylaluminum hydrides, such as
10 dimethylaluminum hydride, diethylaluminum hydride, dipropylaluminum hydride, diisobutylaluminum hydride, dihexylaluminum hydride, dioctylaluminum hydride, and didecylaluminum hydride, alkoxyaluminum hydrides, such as methoxymethylaluminum hydride, methoxyethylaluminum
15 hydride, methoxyisobutylaluminum hydride, ethoxyhexylaluminum hydride, ethoxyoctylaluminum hydride, and ethoxydecylaluminum hydride, and alkylaluminum alkoxides, such as dimethylaluminum methoxide, methylaluminum dimethoxide, diethylaluminum methoxide, ethylaluminum
20 dimethoxide, diisobutylaluminum methoxide, isobutylaluminum dimethoxide, dihexylaluminum methoxide, hexylaluminum dimethoxide, dimethylaluminum ethoxide, methylaluminum diethoxide, diethylaluminum ethoxide, ethylaluminum diethoxide, diisobutylaluminum ethoxide,
25 and isobutylaluminum diethoxide.

Preferred of such compounds from the viewpoint of catalytic activity are trialkylaluminums, which are compounds of the formula wherein a is 3, such as



1 trimethylaluminum, triethylaluminum, tripropylaluminum,
triisobutylaluminum, trihexylaluminum, and the like.
However, the present invention is not limited to the
above-mentioned compounds.

5 Specific examples of aluminoxanes (B2)
represented by the formula $-[Al(R^{11})-O]_n-$ include
tetramethyldialuminoxane, tetraethyldialuminoxane,
tetrabutylaluminoxane, tetrahexyldialuminoxane,
methyldialuminoxane, ethyldialuminoxane, butyldialuminoxane
10 and hexyldialuminoxane. The present invention,
however, is not limited to the above-mentioned compounds.

 The component (B) may be used in a wide range
such as usually 0.01-10,000 moles relative to 1 mole of
titanium atom of the component (A), but it is preferably
15 used in the range of 0.05-500 moles, more preferably
0.1-50 moles, relative to 1 mole of titanium atom.

 Next, the synthesis of the reaction product (A)
in the present invention is described below.

 The reaction product (A), namely one of the
20 catalyst components in the present invention, can be
prepared by reacting a titanium compound (A1) with an
organometallic compound (A2). When the reaction product
thus obtained contains a solid, it is preferable that the
reaction product is used in the form of slurry, or the
25 solid is removed by filtration and the resulting liquid
alone is used for polymerization. The use of the solid
alone is not preferable because the solid formed has a
very low catalytic activity as compared with the liquid



1 component and further gives copolymers having a wide composition distribution.

The reaction of the titanium compound (A1) with the organometallic compound (A2) may be effected either
5 by adding the organometallic compound (A2) to the titanium compound (A1) or by adding the titanium compound (A1) to the organometallic compound (A2).

The reaction temperature is usually in the range of -50 to 230°C, preferably 0 to 200°C. The
10 reaction time is not particularly restricted, but usually 1 minutes to 2 hours.

The amount of the organometallic compound (A2) used is, in terms of the atomic ratio of the metal in the organometallic compound (A2) to the titanium in the
15 titanium compound (A1), in the range of usually 0.01-100, preferably 0.05-50, more preferably 0.1-10.

The catalyst components and the catalyst according to the present invention are used for producing ethylene- α -olefin copolymers. Said copolymers herein
20 refer to copolymers formed from ethylene and one or more α -olefin.

Specific examples of the α -olefin include α -olefins having 3-30 carbon atoms, such as propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1,
25 octene-1, decene-1, octadecene-1, and eicosene-1.

Further, dienes may also be copolymerized in order to improve the vulcanizability of the copolymer. Specific examples of such dienes include 1,3-butadiene,



1 dicyclopentadiene, tricyclopentadiene, 5-methyl-2,5-
norbornadiene, 5-methylene-2-norbornene, 5-ethyldiene-2-
norbornene, 5-isopropenyl-2-norbornene, 5-(2'-butenyl)-
2-norbornene, 1,5,9-cyclododecatriene, 6-methyl-4,7,8,9-
5 tetrahydroindene, trans-1,2-divinylcyclobutane, 1,4-
hexadiene, 4-methyl-1,4-hexadiene, 1,3-hexadiene, 1,6-
octadiene, and 6-methyl-1,5-heptadiene. The present
invention, however, is not to be limited to the above
compounds.

10 The copolymer obtained according to the present
invention can have a density in the range of 0.85-0.95
g/cm³, but preferably has a density in the range of
0.88-0.95 g/cm³, more preferably 0.90-0.95 g/cm³.

An example of the process for producing
15 ethylene- α -olefin copolymers using the catalyst
components or the catalyst according to the present
invention is described below.

The method for feeding the respective catalyst
components to the polymerization vessel is subject to no
20 particular restriction except that they should be fed in
an inert gas, such as nitrogen or argon, and in the
absence of moisture. The catalyst components (A) and (B)
may be either fed each individually or fed after having
been made to contact with each other in advance.

25 The polymerization temperature may be usually
in the range of -30 to 300°C, but is preferably 0 to
280°C, more preferably 20 to 250°C.

The polymerization pressure is not particularly



1 restricted, but preferably about 3-1500 atm from the
viewpoint of industrial practicality and economical
efficiency.

The polymerization can be conducted either
5 continuously or batchwise. It may be slurry or solution
polymerization which use an inert hydrocarbon solvent,
such as propane, butane, pentane, hexane, and octane, or
liquid phase or gas phase polymerization which use no
solvent.

10 Further, a chain transfer agent, such as
hydrogen, may be added to the polymerization system in
order to control the molecular weight of the copolymer of
the present invention.

According to the present invention, a catalyst
15 having a high catalytic activity per unit weight of
transition metal is obtained, whereby productivity can
be improved and further the production of ethylene- α -
olefin copolymers having a high molecular weight and
narrow composition distribution becomes possible; thus,
20 ethylene- α -olefin copolymers excellent in weather
resistance, color development, transparency, corrosive-
ness, and mechanical properties can be provided.

The present invention will be described further
in detail below with reference to Examples and
25 Comparative Examples.

The polymer properties described in Examples
were determined by the following methods.

The α -olefin content was determined from the



- 1 characteristic absorptions of ethylene and α -olefin
measured by using an infrared spectrophotometer (JASCO-
302, mfd. by NIPPON BUNKO KOGYO CO.).

The intrinsic viscosity $[\eta]$ was determined by
5 using an Ubbelohde's viscometer in tetralin solution at
135°C.

As the measure for representing composition
distribution, an average melting point $\langle T_m \rangle$ defined by
the following equation was determined by using a
10 differential scanning calorimeter (DSC). The smaller
 $\langle T_m \rangle$ value indicates the narrower composition distribu-
tion.

$$\langle T_m \rangle = \frac{\sum (H_i \times t_i)}{\sum H_i}$$

wherein $50^\circ\text{C} < t_i < 120^\circ\text{C}$, and H_i denotes the melting
energy (w/g) at temperature t_i .

15 Example 1

(1) Synthesis of reaction product (A)

Synthesis of titanium compound (A1):

A 300-ml flask equipped with a stirrer,
dropping funnel and thermometer was purged with argon
20 gas, and 18.1 ml (60 mmols) of dioctylamine and 150 ml of
hexane were charged therein.

Then, 38.7 ml (60 mmols) of n-butyllithium
diluted with hexane was added dropwise from the dropping



1 funnel over a period of 30 minutes with stirring while
keeping the temperature of the solution in the flask at
5°C. After completion of the addition, the reaction was
further conducted at 5°C for 2 hours and at 30°C for 2
5 hours.

Then, 2.2 ml (20 mmols) of TiCl_4 diluted with
hexane was added dropwise from the dropping funnel to the
liquid mixture obtained by the above reaction over a
period of 30 minutes while keeping the temperature of the
10 liquid mixture at 5°C. After completion of the addition,
the reaction was further continued at 5°C for 1 hour and
at 30°C for 2 hours, to obtain 20 mmols (as 100% yield)
of a titanium compound (A-1) represented by the compo-
sition formula $[(\text{C}_8\text{H}_{17})_2\text{N}]_3\text{TiCl}$.

15 Reaction of titanium compound (A1) with organometallic
compound (A2):

To the reaction product obtained above was
added 30 ml (19.8 mmols) of butylethylmagnesium
(hereinafter abbreviated as BEM) (mfd. by Tosoh-Akzo Co.)
20 diluted with heptane, and the resulting mixture was
allowed to react for 1 hour while keeping the temperature
at 30°C, to obtain 20 mmols of a reaction product (A)
(hereinafter called "component (A)"). (catalyst
concentration: 0.077 mmol Ti/ml).

25 (2) Polymerization of ethylene

An autoclave of 400-ml inner volume equipped



1 with a stirrer and a thermometer was dried under vacuum
and purged with argon gas. Then, 100 ml of toluene as a
solvent and 800 mmols of hexene-1 as an α -olefin were
charged therein, and the reactor was heated up to 180°C.
5 Thereafter, ethylene was fed into the reactor while
adjusting the ethylene pressure to 25 kg/cm². After the
reaction system had become stable, 0.1 mmol of triethyl-
aluminum (hereinafter abbreviated as TEA) was fed as the
organoaluminum compound (B) and succeedinglly 0.063 mmol
10 of the component (A) synthesized in (1) above was fed
into the reactor. Then polymerization was conducted for
2 minutes while controlling the temperature at 180°C. As
the result of the polymerization, 47,000 g of copolymer
was obtained per 1 mol of transition metal (activity:
15 47,000 g-copolymer/mol. M). The results are shown in
Table 1. The melting behavior of the copolymer obtained
was determined with a DSC and the resulting diagram is
shown in Fig. 1. In Fig. 1, the numbers on the abscissa
indicate the temperature (°C) and those on the ordinate
20 indicate the melting energy (mW). In Fig. 1, as the
melting peak is recognized at the lower temperature side,
the composition distribution tends to be the narrower.
The composition distribution of the copolymer obtained
was shown to be very narrow.

25 Example 2

A reaction product was synthesized in the same
manner as in the synthesis of the reaction product (A) of



- 1 Example 1(1) except that dihexylmagnesium (abbreviated as
DHM) made by Tosoh-Akzo Co.) was used in place of BEM,
and then ethylene was polymerized in the same manner as
in Example 1 except that the reaction product obtained
5 above was used in place of the reaction product (A) of
Example 1. The results are shown in Table 1. A polymer
having a narrow composition distribution was obtained as
in Example 1.

Example 3

10 Polymerization of ethylene

- An autoclave of 400-ml inner volume equipped
with a stirrer and a thermometer was dried under vacuum
and purged with argon gas. Then, 82 g of butane as a
solvent and 321 mmols of butene-1 as an α -olefin were
15 charged therein, and the reactor was heated up to 70°C.
Thereafter, hydrogen and ethylene were fed into the
reactor while adjusting the hydrogen pressure to 1.0
kg/cm² and the ethylene pressure to 6.0 kg/cm². After
the reaction system had become stable, 0.25 mmol of TEA
20 was fed as the organoaluminum compound (B), and
succeedingly 0.16 mmol of the component (A) synthesized
in Example 1(1) was fed into the reactor. Then,
polymerization was conducted for 60 minutes while
controlling the temperature at 70°C. The results are
25 shown in Table 1. A polymer having a narrow composition
distribution was obtained as in Example 1 (see Fig. 2).



1 Comparative Example 1.

Ethylene was polymerized in the same manner as in Example 3 except that 0.16 mmol of a titanium compound (A1) represented by the composition formula

5 $[(C_8H_{17})_2N]_3TiCl$ was used in the polymerization in place of the component (A). The results are shown in Table 1. The results of polymerization showed that the catalytic activity was low and the polymer obtained had a wide composition distribution (see Fig. 3).

10 Example 4

(1) Synthesis of reaction product (A)

Synthesis of titanium compound (A1):

A 300-ml flask equipped with a stirrer, dropping funnel and thermometer was purged with argon

15 gas, and then 6.3 ml (60 mmols) of diethylamine and 150 ml of hexane were charged therein.

Then, 38.7 ml (60 mmols) of n-butyllithium diluted with hexane was added dropwise from the dropping funnel over a period of 30 minutes while keeping the

20 temperature of the solution in the flask at 5°C. After completion of the addition, the reaction was further conducted at 5°C for 2 hours and at 30°C for 2 hours.

Subsequently, 3.3 ml (30 mmols) of $TiCl_4$ diluted with hexane was added dropwise from the dropping

25 funnel to the liquid mixture obtained by the above reaction over a period of 30 minutes while keeping the temperature at 5°C. After completion of the addition,



1 the reaction was further conducted at 5°C for 1 hour and
at 30°C for 2 hours, to obtain 30 mmols (as 100% yield)
of a titanium compound (A1) represented by the composi-
tion formula $[(C_2H_5)_2N]_2TiCl_2$.

5 Reaction of titanium compound (A1) with organometallic
compound (A2):

To the reaction product obtained above was
added 45.5 ml (30 mmols) of butylethylmagnesium (BEM)
(mfd. by Tosoh-Akzo Co.) diluted with heptane, and the
10 resulting mixture was allowed to react for 1 hour while
keeping the temperature at 30°C, to obtain 21.2 mmols of
a reaction product (A) (catalyst concentration 0.112
mmol Ti/ml).

(2) Polymerization of ethylene

15 Polymerization was conducted in the same manner
as in Example 1(2) except that 0.063 mmol of the
component (A) synthesized in (1) above was used as the
reaction product (A) and 0.1 mmol of triisobutylaluminum
(abbreviated as TIBA) was used as the organoaluminum
20 compound (B). The results are shown in Table 1. A
polymer having a narrow composition distribution was
obtained as in Example 1.

Comparative Example 2

Polymerization was conducted in the same manner
25 as in Example 4 except that 0.063 mmol of a titanium



1 compound represented by the composition formula
[(C₂H₅)₂N]₂TiCl₂ was added in place of the component (A)
used in ethylene polymerization of Example 4(2). The
results are shown in Table 1. The result of polymeri-
5 zation showed a very low activity of the catalyst.

Example 5

Polymerization was conducted in the same manner
as in Example 1 except that 0.1 mmol of trihexylaluminum
(abbreviated as THA) was added as the organoaluminum
10 compound in place of TEA used in ethylene polymerization
of Example 1(2). The results of polymerization are shown
in Table 1. A polymer having also a narrow composition
distribution was obtained as in Example 1.

Example 6

15 A reaction product was prepared in the same
manner as in Example 3 except that MAGALA 7.5E (a trade
name, composition formula: 7.5(n-C₄H₉)₂Mg•(C₂H₅)Al, mfd.
by Tosoh-Akzo Co.) was used in place of BEM used in the
synthesis of the reaction product (A) of Example 3(1),
20 and then ethylene was polymerized in the same manner as
in Example 3 except that the reaction product prepared
above was used. The results are shown in Table 1. The
polymerization yielded a polymer having a narrow
composition distribution as in Example 3.



Table 1

	Reaction product (A)		Organo-aluminum compound (B)	Polymerization temp. (°C)	Activity ($\frac{\text{g-Copolymer}}{\text{mol. M}}$)	*1) Comonomer content (wt.%)	[η]	<T _m > (°C)
	Titanium compound	*2) Organo-metallic compound						
Example 1	$[(\text{C}_8\text{H}_{17})_2\text{N}]_3\text{TiCl}$	BEM	TEA	180	47000	10.4	0.55	98.4
Example 2	"	DHM	"	"	23000	9.2	0.63	98.5
Example 3	"	BEM	"	70	68000	10.0	1.53	94.4
Comp. Example 1	"	—	"	"	9200	7.6	2.75	103.8
Example 4	$[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{TiCl}_2$	BEM	TIBA	180	6300	6.6	0.66	98.7
Comp. Example 2	"	—	"	"	940	—	—	—
Example 5	$[(\text{C}_8\text{H}_{17})_2\text{N}]_3\text{TiCl}$	BEM	THA	"	43000	10.9	0.60	97.9
Example 6	"	7.5E	TEA	70	36000	8.8	1.51	99.6

Note: *1) Comonomer is hexene-1, except for butene-1 in Examples 3 and 6 and Comparative Example 1.

*2) BEM: $(n\text{-C}_4\text{H}_9)\text{Mg}(\text{C}_2\text{H}_5)$ DHM: $(n\text{-C}_6\text{H}_{13})_2\text{Mg}$ 7.5E: $7.5(n\text{-C}_4\text{H}_9)_2\text{Mg} \cdot (\text{C}_2\text{H}_5)_3\text{Al}$
 TEA: $(\text{C}_2\text{H}_5)_3\text{Al}$ THA: $(n\text{-C}_6\text{H}_{13})_3\text{Al}$ TIBA: $[(\text{CH}_3)_2\text{CHCH}_2]_3\text{Al}$



1 Example 7

(1) Synthesis of reaction product (A)

A reaction product (A) was synthesized in the same manner as in Example 1 except that 12.0 ml of a 1.67
5 mol/l hexane solution of n-butyllithium was used in place of BEM diluted with heptane used in the synthesis of the reaction product (A) of Example 1(1), to obtain 20 mmols of the reaction product (A) (catalyst concentration: 0.087 mmolTi/ml).

10 (2) Copolymerization of ethylene with butene-1

An autoclave of 3000-ml inner volume equipped with a stirrer and a thermometer was dried under vacuum and purged with argon gas. Then, hydrogen to a pressure of 300 mmHg, 765 g of butane as a solvent and 140 g of
15 butene-1 as an α -olefin were charged into the reactor, and the reactor was heated up to 70°C. Thereafter, ethylene was fed to the reactor while adjusting the ethylene pressure to 6 kg/cm². After the reaction system had become stable, 1.6 mmols of triethylaluminum (TEA)
20 was fed as the organoaluminum compound (B), succeedingly 0.39 mmol of the component (A) synthesized in (1) above was fed into the reactor, and polymerization was conducted for 2 hours while controlling the temperature at 70°C. As the result of the polymerization, 30.0 g of
25 a copolymer was obtained (activity: 76,900 g-copolymer/mol·Ti·hr). The results are shown in Table 2. The melt index of the copolymer obtained was determined according



1 to JIS K-6760 at 190°C. The melting behavior of the
copolymer was determined with a DSC and the resulting
diagram is shown in Fig. 4. In Fig. 4, the numbers on
the abscissa indicate the temperature (°C), and those on
5 the ordinate indicate the melting energy. In Fig. 4, as
the melting peak is recognized at the lower temperature
side, the composition distribution tends to be the
narrower. The composition distribution of the copolymer
obtained was shown to be very narrow.

10 Example 8

Copolymerization of ethylene with butene-1 was
conducted in the same manner as in Example 7 except that
20 mmols of sec-butyllithium was used in place of n-BuLi
in the synthesis of the component (A), and the component
15 (A) thus obtained was used in the copolymerization. As
result, 21.0 g of a copolymer was obtained (activity:
53,900). The results thus obtained are shown in Table 2
and Fig. 5.



Table 2

	Reaction product (A)		Organo- aluminum compound (B)	Activity g-polymer mol·Ti·hr	Comonomer content (wt. %)	MI	<T _m > (°C)
	Titanium compound	Organo- metallic compound					
Example 7	$[(C_8H_{17})_2N]_3TiCl$	n-BuLi	TEA	76,900	8.6	5.8	95.1
Example 8	$[(C_8H_{17})_2N]_3TiCl$	sec-BuLi	TEA	53,900	7.9	4.9	95.6

- 49 -

This Sheet Has Been Replaced



1 Example 9

(1) Synthesis of reaction product (A)

Synthesis of titanium compound (A1):

A 300-ml flask equipped with a stirrer,
5 dropping funnel and thermometer was purged with argon gas, and 18.1 ml (60 mmols) of dioctylamine and 150 ml of hexane were charged therein.

Then, 38.7 ml (60 mmols) of n-butyllithium diluted with hexane was added dropwise from the dropping
10 funnel over a period of 30 minutes while keeping the temperature of the solution in the flask at 5°C. After completion of the addition, the reaction was further conducted at 5°C for 2 hours and at 30°C for 2 hours.

Then, 1.65 ml (15 mmols) of TiCl_4 diluted with
15 hexane was added dropwise from the dropping funnel to the liquid mixture obtained in the above reaction over a period of 30 minutes while keeping the temperature of the liquid mixture at 5°C. After completion of the addition, the reaction was further conducted at 5°C for 1 hour and
20 at 30°C for 2 hours, to obtain 15 mmols (as 100% yield) of a titanium compound (A1) represented by the composition formula $[(\text{C}_8\text{H}_{17})_2\text{N}]_4\text{Ti}$.

Reaction of titanium compound (A1) with organometallic compound (A2):

25 To the titanium compound obtained above was added 30 ml (30 mmols) of triethylaluminum (A2) diluted with hexane, and the resulting mixture was allowed to



1 react for 1 hour while keeping the temperature at 30°C to
obtain 10.5 mmols of a reaction product (A) (catalyst
concentration: 0.062 mmol Ti/ml).

(2) Polymerization of ethylene

5 An autoclave of 400-ml inner volume equipped
with a stirrer and a thermometer was dried under vacuum
and purged with argon gas. Then, 100 ml of toluene as a
solvent and 800 mmols of hexene-1 as an α -olefin were
charged therein, and the reactor was heated up to 180°C.
10 Thereafter, ethylene was fed into the reactor while
adjusting the ethylene pressure to 25 kg/cm². After the
reaction system had become stable, 0.5 mmol of
triethylaluminum (TEA) was fed as the organoaluminum
compound (D), and successingly 0.32 mmol of the component
15 (A) synthesized in (1) above was fed into the reactor.
Then, polymerization was conducted for 2 minutes while
controlling the temperature at 180°C. As the result of
the polymerization, 8750 g of a copolymer was obtained
per 1 mol of transition metal (activity: 8750 g-copolymer/
20 mol·M). The results are shown in Table 3. The melting
behavior of the copolymer obtained was determined with a
DSC and the resulting diagram is shown in Fig. 6. In
Fig. 6, the numbers on the abscissa indicate the
temperature (°C) and those on the ordinate indicate the
25 melting energy (μ W). In Fig. 6, as the melting peak is
recognized at the lower temperature side, the composition
distribution tends to be the narrower. The $\langle T_m \rangle$



1 determined from Fig. 6 was 98.1°, revealing that the
copolymer obtained had a very narrow composition
distribution.

Comparative Example 3

5 Polymerization was conducted in the same manner
as in Example 9 except that 47 mmols of diethylaluminum
chloride (abbreviated as DEAC) was used as the organo-
metallic compound in place of TEA used in the reaction of
10 a titanium compound (A1) with an organometallic compound
(A2) in the synthesis of a reaction product (A) of
Example 9(1) and that no TEA was added in the polymeriza-
tion of ethylene of (2) above. The results are shown in
Table 3. The catalytic activity was very low as compared
with that in Example 9.

15 Example 10

Polymerization of ethylene

An autoclave of 400-ml inner volume equipped
with a stirrer and a thermometer was dried under vacuum
and purged with argon gas. Then, 75 g of butane as a
20 solvent and 446 mmols of butene-1 as an α -olefin were
charged therein, and the reactor was heated up to 70°C.
Then, hydrogen and ethylene were fed into the reactor
while adjusting the hydrogen pressure to 0.5 kg/cm² and
the ethylene pressure to 6.0 kg/cm². After the reaction
25 system had become stable, 0.5 mmol of TEA was fed as the
organoaluminum compound (B) and succeedingly 0.32 mmol of



1 the component (A) synthesized in Example 9(1) was fed
into the reactor. Then, polymerization was conducted for
60 minutes while controlling the temperature at 70°C.
The results are shown in Table 3. A polymer having a
5 narrow composition distribution was obtained as in
Example 9 (see Fig. 7).

Comparative Example 4

Polymerization was conducted in the same manner
as in Example 10 except that, in the ethylene polymeri-
10 zation of Example 9(2), 0.25 mmol of triethylaluminum
(TEA) was used as the organoaluminum compound (B) and
0.16 mmol of a titanium compound represented by the
composition formula $[\text{C}_8\text{H}_{17})_2\text{N}]_3\text{TiCl}$ was used in place of
the component (A). The results thus obtained are shown
15 in Table 3. As the result of polymerization, the
catalytic activity was lower and the composition
distribution of the resulting polymer was wider than in
Example 10 (see Fig. 8).

Example 11

20 Polymerization was conducted in the same manner
as in Example 9 except that 0.5 mmol of trihexylaluminum
(THA) was used as the organoaluminum compound (B) in
place of TEA used in the ethylene polymerization of
Example 9(2). The results of polymerization are shown in
25 Table 3. A polymer having also a narrow composition
distribution was obtained as in Example 9.



1 Example 12

(1) Synthesis of reaction product (A)

Synthesis of titanium compound (A1):

A 300-ml flask equipped with a stirrer,
5 dropping funnel and thermometer was purged with argon
gas, and 6.3 ml (60 mmols) of diethylamine and 150 ml of
hexane were charged therein.

Then, 38.7 ml (60 mmols) of n-butyllithium
diluted with hexane was added dropwise from the dropping
10 funnel over a period of 30 minutes while keeping the
temperature of the solution in the flask at 5°C. After
completion of the addition, the reaction was further
conducted at 5°C for 2 hours and at 30°C for 2 hours.

Then, 1.65 ml (15 mmols) of TiCl_4 diluted with
15 hexane was added dropwise from the dropping funnel to the
liquid mixture obtained in the above reaction over a
period of 30 minutes while keeping the temperature at
5°C. After completion of the addition, the reaction was
further conducted at 5°C for 1 hour and at 30°C for 2
20 hours to obtain 15 mmols (as 100% yield) of a titanium
compound (A1) represented by the composition formula
 $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{Ti}$.

Reaction of titanium compound (A1) with organometallic
compound (A2):

25 To the reaction mixture obtained above was
added 30 ml (30 mmols) of triethylaluminum diluted with
hexane, and the resulting mixture was allowed to react



1 for 1 hour while keeping the temperature at 30°C, to
obtain 11.0 mmols of a reaction product (A) (catalyst
concentration: 0.063 molTi/ml.)

(2) Polymerization of ethylene

5 Polymerization was conducted in the same manner
as in Example 9(2) except that 0.32 mmol of the component
(A) synthesized in (1) above was used as the reaction
product (A). The results are shown in Table 3. A
polymer having a narrow composition distribution was
10 obtained as in Example 9.

Comparative Example 5

Polymerization was conducted in the same manner
as in Example 12 except that, in the polymerization of
ethylene of Example 12(2), 1.1 mmols of TEA was used and
15 0.32 mmol of a titanium compound $[(C_2H_5)_2N]_4Ti$ synthe-
sized in the same manner as in Example 12(1) was used in
place of the component (A). The results of polymer-
ization are shown in Table 3. The catalytic activity was
low as compared with that in Example 12.

20 Example 13

A reaction product (A) was synthesized in the
same manner as in Example 9 except that triisobutyl-
aluminum (TIBA) was used in place of TEA in the synthesis
of the reaction product (A) of Example 9(1) and then
25 polymerization was conducted in the same manner as in



1 Example 9 except that the reaction product (A) synthesized above was used. The results are shown in Table 3. A polymer having a narrow composition distribution was obtained as in Example 9.

5 Example 14

A reaction product (A) was synthesized in the same manner as in Example 9 except that methylaluminoxane (abbreviated as MAO) (mfd. by Tosoh-Akzo Co.) was used in place of TEA in the synthesis of the reaction product (A)
10 of Example 9(1), and then polymerization was conducted in the same manner as in Example 9 except that the reaction product synthesized above was used. The results are shown in Table 3. A polymer having a narrow composition distribution was obtained as in Example 9.

15 Example 15

Polymerization was conducted in the same manner as in Example 9 except that 1 g of 1,3-butadiene was further added in the polymerization of Example 9(2). The results are shown in Table 3. The polymer obtained
20 showed an iodine value of 21.2. The iodine value was obtained from the characteristic absorption of diene determined by using an infrared spectrophotometer (JASCO-302, mfd. by NIPPON BUNKO KOGYO CO.).

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Table 3

	Reaction product (A)		Organo-aluminum compound (B)	Polymerization temp. (°C)	Activity g-Copolymer mol. M	*1) Comonomer content (wt.%)	[η]	<Tm> (°C)
	Titanium compound	*2) Organo-metallic compound						
Example 9	$[(C_8H_{17})_2N]_4Ti$	TEA	TEA	180	8750	10.4	0.67	98.1
Comp. Example 3	"	DEAC	—	"	150	8.1	—	—
Example 10	"	TEA	TEA	70	32000	9.0	1.81	97.6
Comp. Example 4	$[C_8H_{17})_2N]_3TiCl$	—	"	"	9200	7.6	2.75	103.8
Example 11	$[(C_8H_{17})_2N]_4Ti$	TEA	THA	180	7300	11.3	0.66	96.3
Example 12	$[(C_2H_5)_2N]_4Ti$	"	TEA	"	7280	12.6	0.60	92.8
Comp. Example 5	"	—	"	"	750	10.4	0.44	98.2
Example 13	$[(C_8H_{17})_2N]_4Ti$	TIBA	"	"	8280	10.2	0.64	98.8
Example 14	"	MAO	"	"	8230	10.1	0.67	98.5
Example 15	"	TEA	"	"	5600	5.0	0.94	99.7

Note: *1) Comonomer is hexene-1, except for butene-1 in Example 10 and Comparative Example 4, and hexene-1 and 1,3-butadiene in Example 15.

*2) TEA: Triethylaluminum DEAC: Diethylaluminum chloride THA: Trihexylaluminum
TIBA: Triisobutylaluminum MAO: Methylaluminoxane



CLAIMS:

1. A catalyst for copolymerizing ethylene with an α -olefin comprising a reaction product (A) of a titanium compound (A1) having at least one titanium-nitrogen bond with an organometallic compound (A2) having at least one element selected from the groups IA, IIA, IIB, IIIA and IVA of the periodic table and an organoaluminum compound (B).
2. The catalyst according to claim 1 wherein the titanium compound (A1) having at least one titanium-nitrogen bond is one which is represented by the formula $(R^1R^2N)_{4-(m+n)}TiX_mY_n$, wherein R^1 and R^2 each denote a hydrocarbon group having 1-30 carbon atoms and may be the same or different, X denotes a halogen, Y denotes an alkoxy group, and m and n are numbers respectively defined by the equations $0 \leq m \leq 3$ and $0 \leq n < 3$, provided that $(m+n)$ is defined by the equation $0 \leq (m+n) \leq 3$.
3. The catalyst according to claim 1, wherein the element selected from the groups IA, IIA, IIB, IIIA and IVA of the periodic table is Li, Na, K, Be, Mg, Ca, Zn, Cd, B, Al, Ga, In or Sn.
4. The catalyst according to claim 1, wherein the organometallic compound (A2) is at least one organometallic compound selected from the group consisting of organolithium compounds, organosodium compounds, organopotassium compounds, organoberyllium compounds, organomagnesium compounds, organocalcium compounds,





organozinc compounds, organocadmium compounds, organoboron compounds, organoaluminum compounds, organogallium compounds, organogallium compounds, organoindium compounds, and organotin compounds.

5. The catalyst according to claim 4, wherein the organometallic compound (A2) is an organomagnesium compound.

6. The catalyst according to claim 5, wherein the organomagnesium compound is at least one organomagnesium compound selected from the group consisting of compounds represented by the following formulas:

(1) R^3R^4Mg , wherein R^3 and R^4 each denote a hydrocarbon group having 1-20 carbon atoms and may be the same or different,

(2) R^5MgZ^1 , wherein R^5 denotes a hydrocarbon group having 1-20 carbon atoms and Z^1 denotes a hydrogen atom or an alkoxy group,

(3) R^6MgX , wherein R^6 denotes a hydrocarbon group having 1-20 carbon atoms and X denotes a halogen.

7. The catalyst according to claim 4, wherein the organometallic compound (A2) is an organolithium compound.

8. The catalyst according to claim 7, wherein the organolithium compound is an organolithium compound represented by the formula R^9Li , wherein R^9 denotes a hydrocarbon group having 1-20 carbon atoms.

9. The catalyst according to claim 4, wherein the organometallic compound (A2) is an organoaluminum



compound.

10. The catalyst according to claim 9, wherein the organoaluminum compound is an organoaluminum compound represented by the formula $R^7_aAlZ^2_{3-a}$, wherein R^7 denotes a hydrocarbon group having 1-20 carbon atoms, Z^2 denotes a hydrogen atom and/or an alkoxy group, and a denotes a number defined by the equation $0 < a \leq 3$, or a chain-like or cyclic aluminoxane having a structure represented by the formula $-[Al(R^8)-O]_l-$, wherein R^8 denotes a hydrocarbon group having 1-20 carbon atoms and l denotes an integer of 1 or more.

11. The catalyst according to claim 1, wherein the organoaluminum compound (B) is an organoaluminum compound (B1) represented by the formula $R^{10}_aAlZ^3_{3-a}$, wherein R^{10} denotes a hydrocarbon group having 1-20 carbon atoms, Z^3 denotes a hydrogen atom and/or an alkoxy group, and a denotes a number defined by the equation $0 < a \leq 3$.

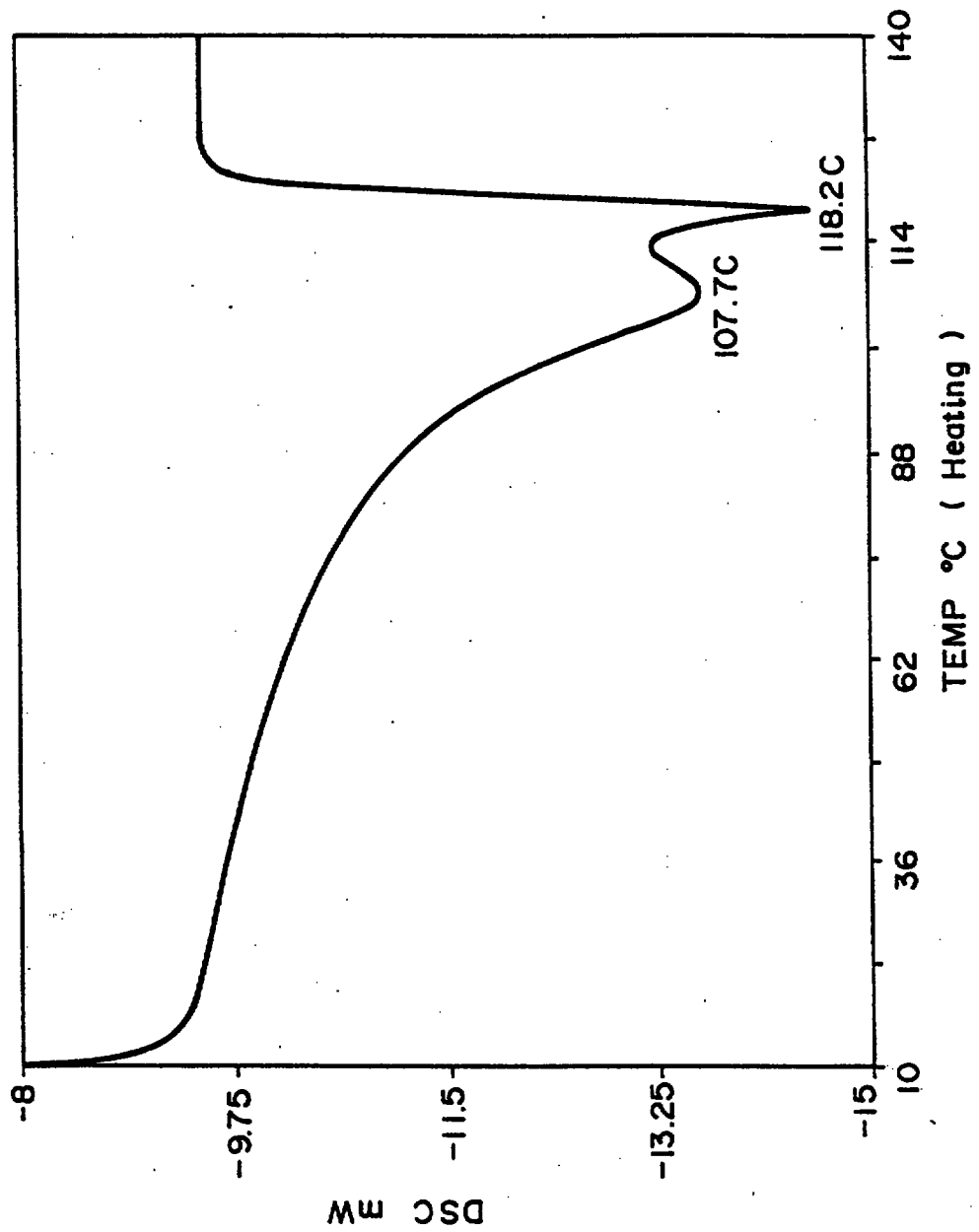
12. Use of a catalyst according to anyone of claims 1 to 11 for producing ethylene- α -olefin copolymers.

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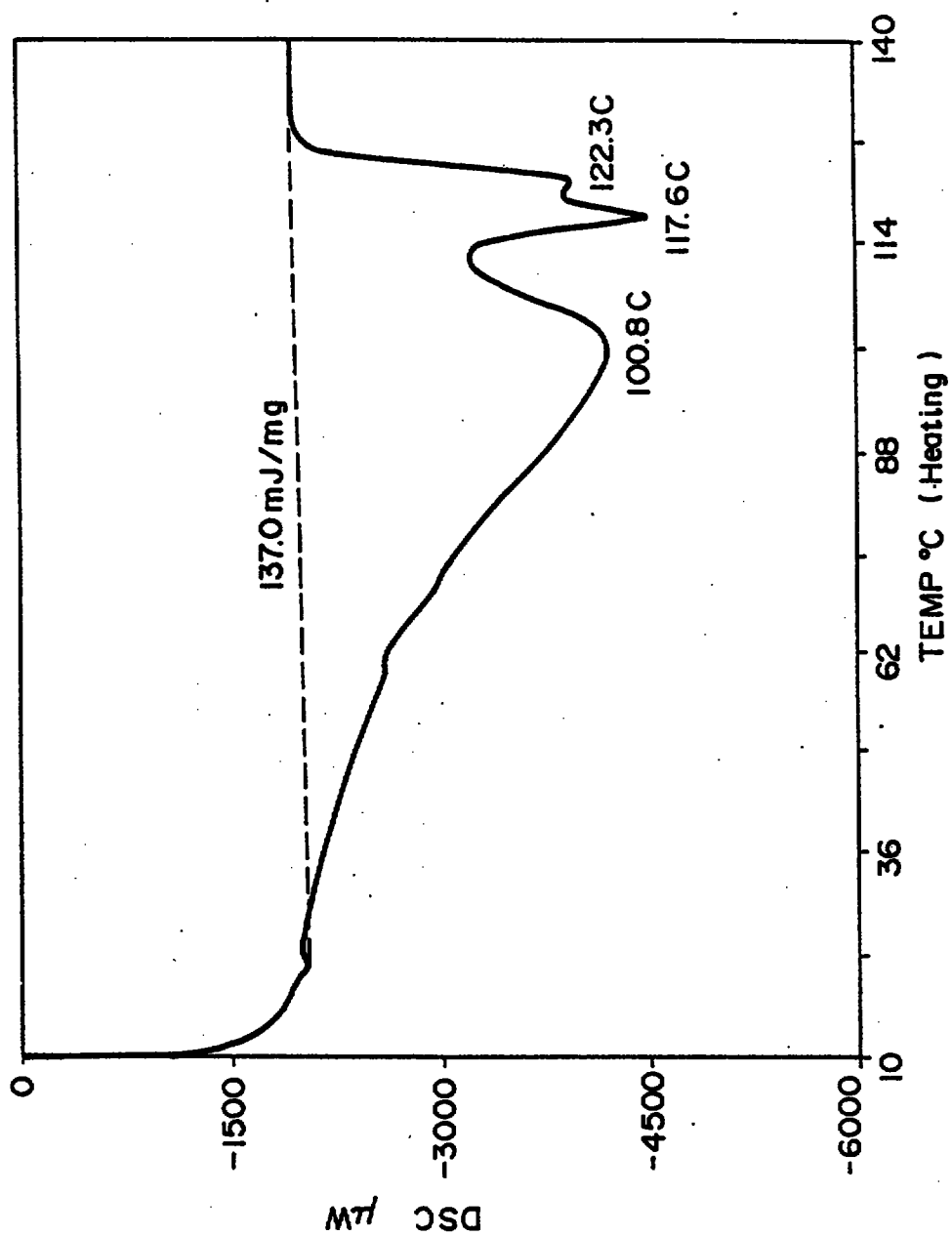
FIG. 1



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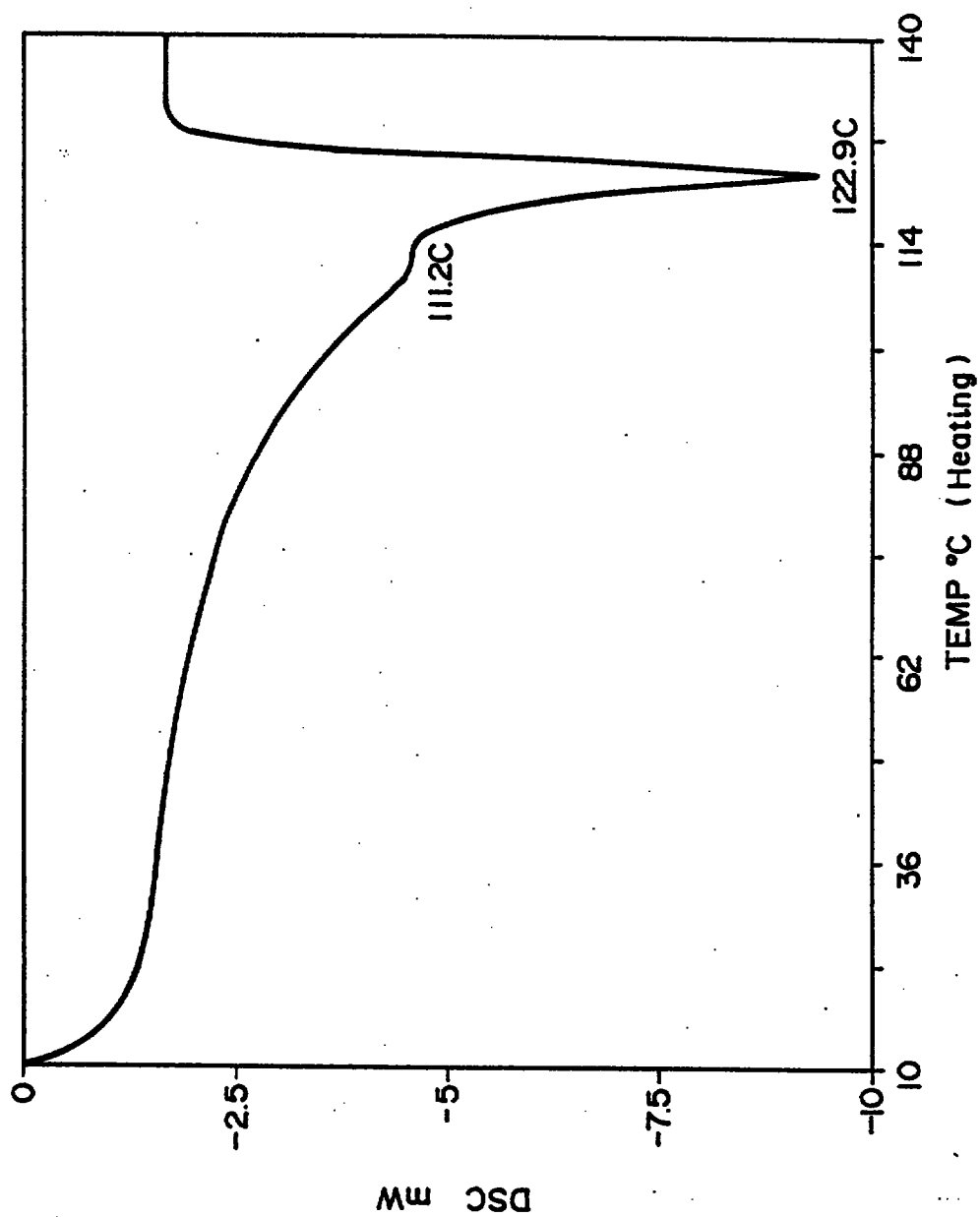
FIG. 2



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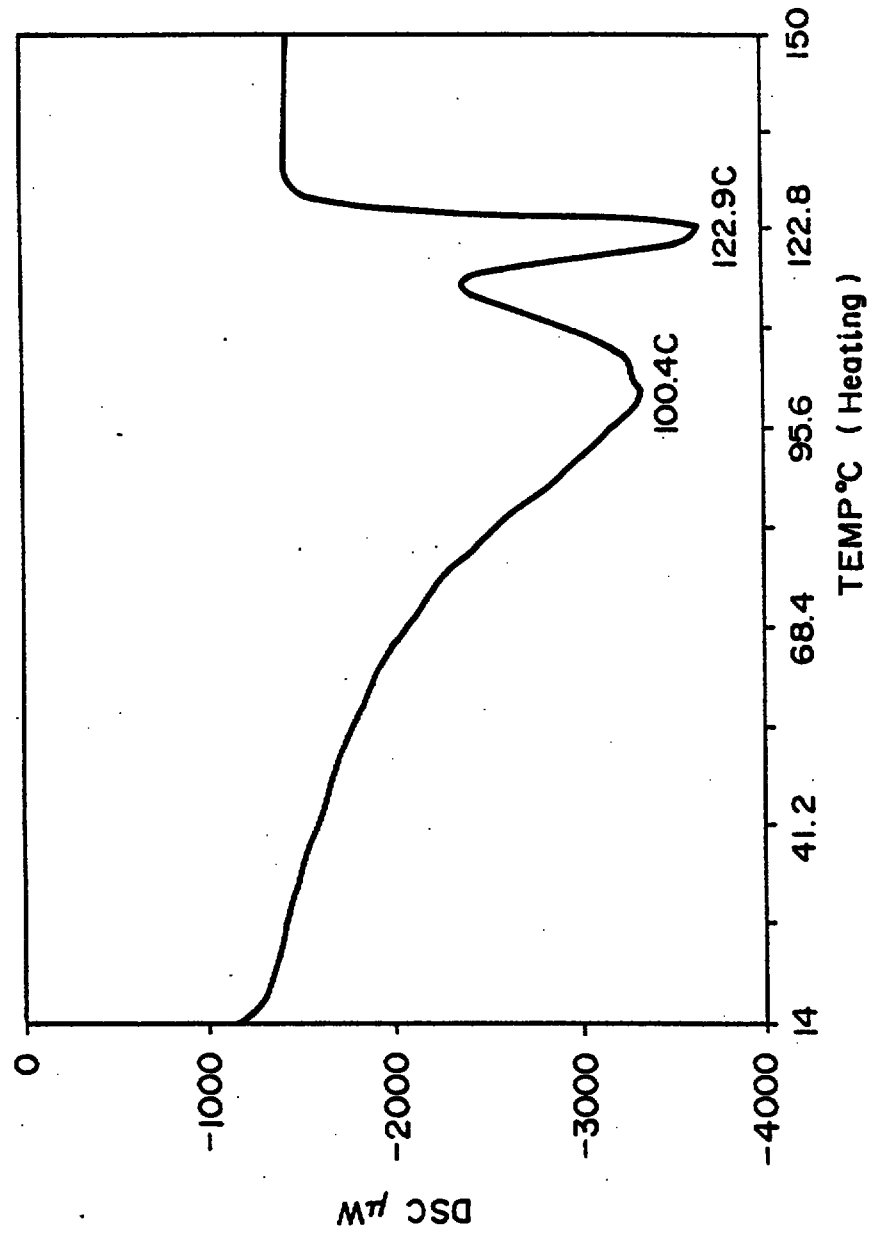
FIG. 3



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FIG. 4



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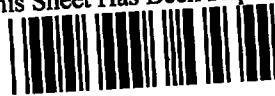
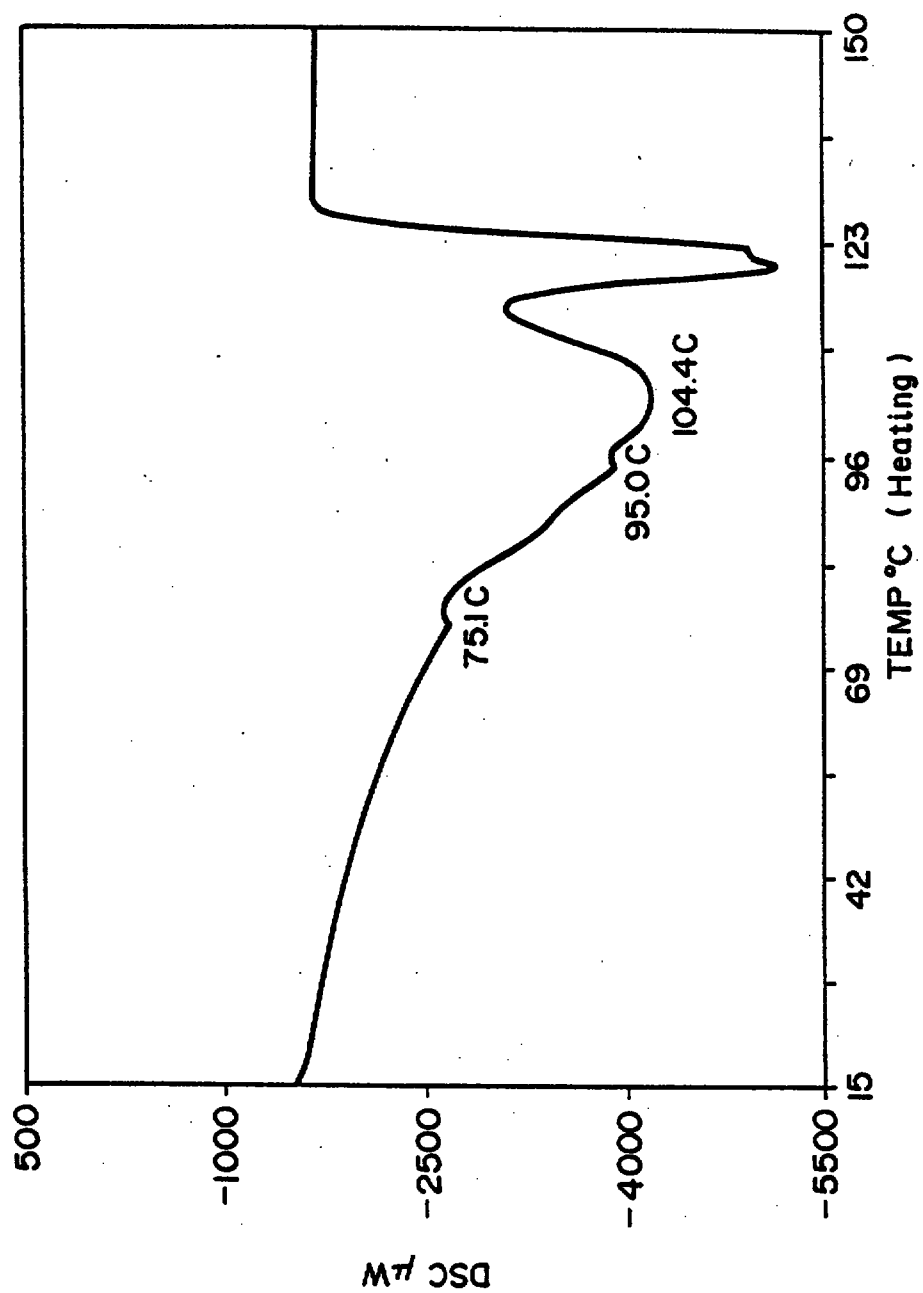


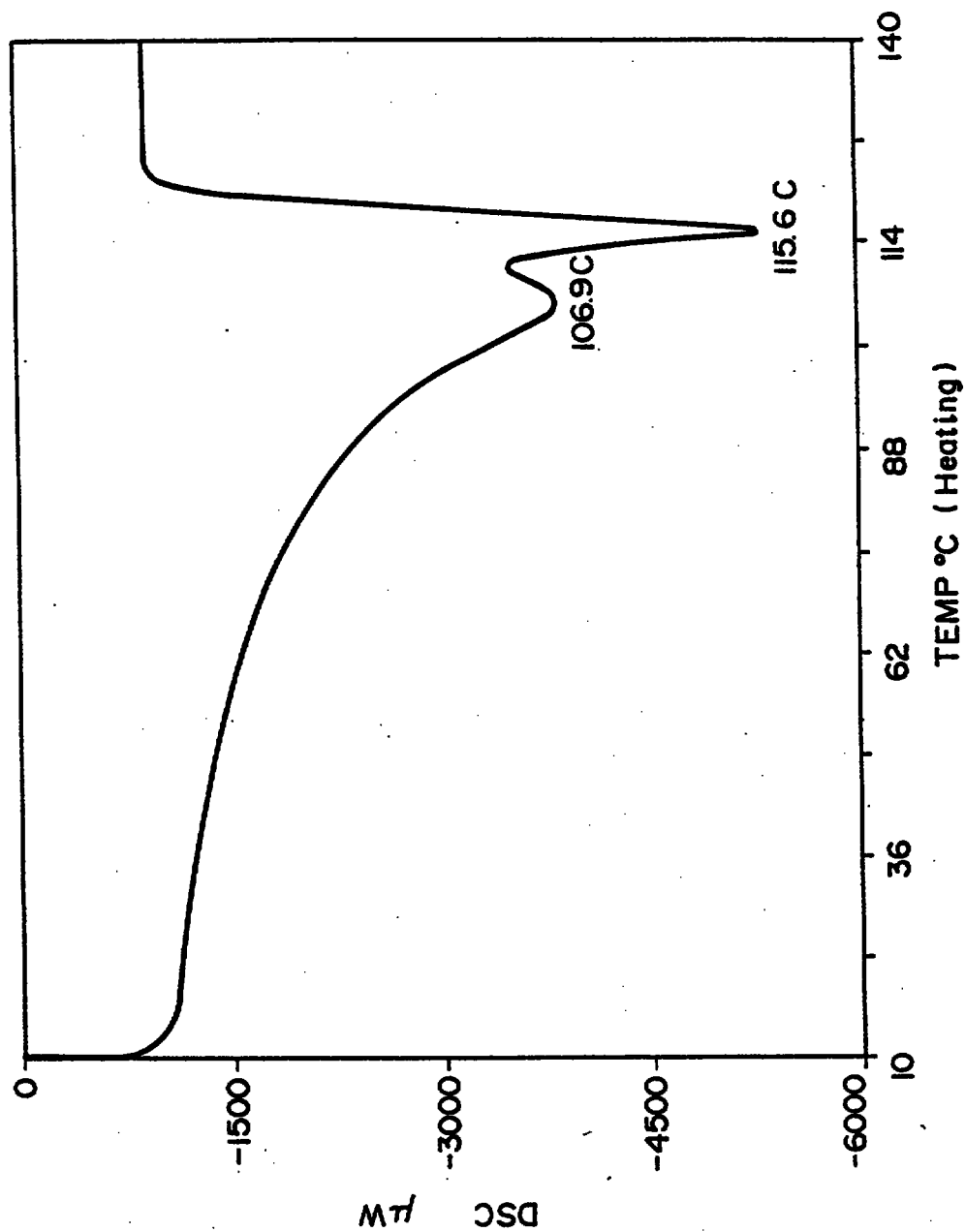
FIG. 5



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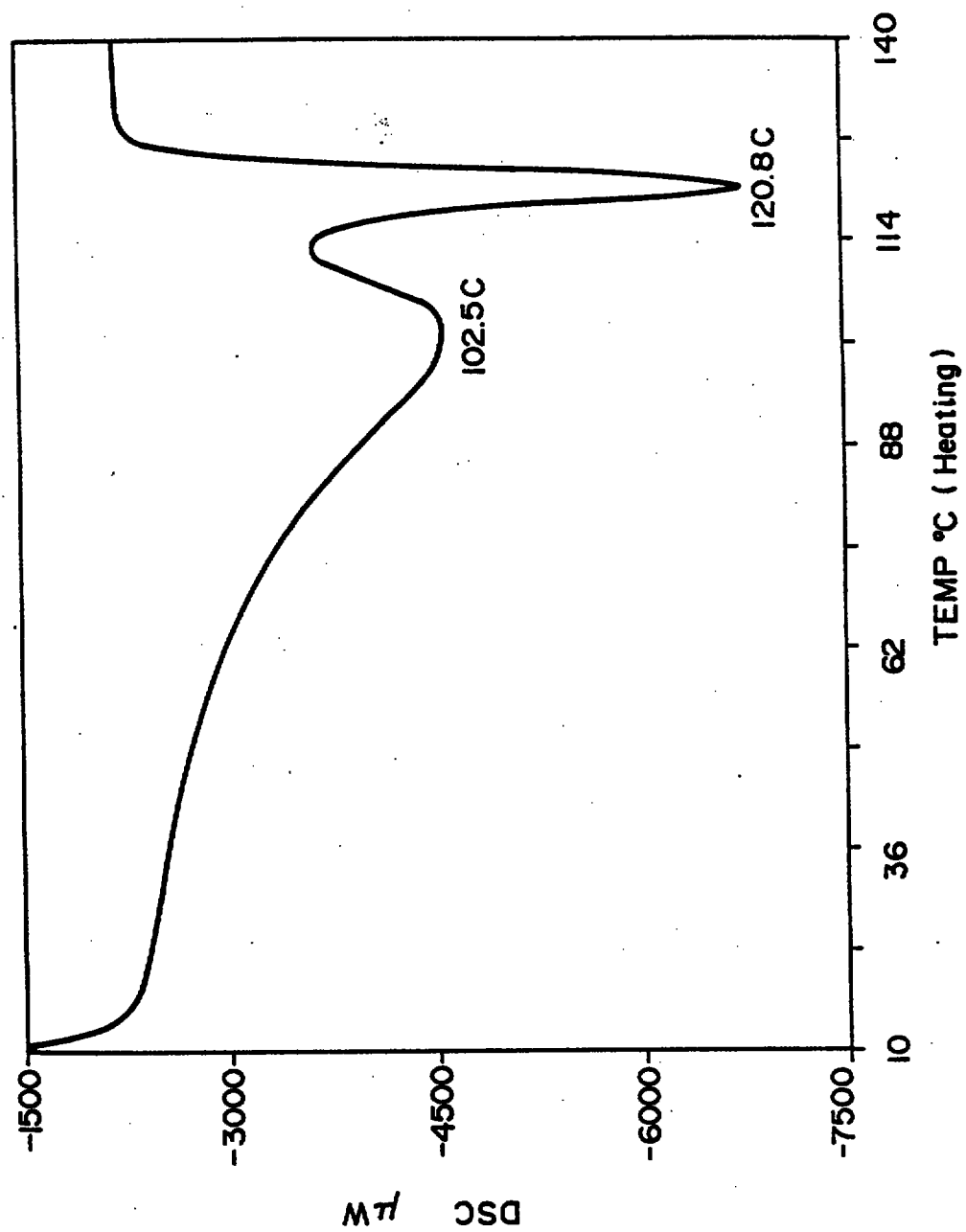
FIG. 6



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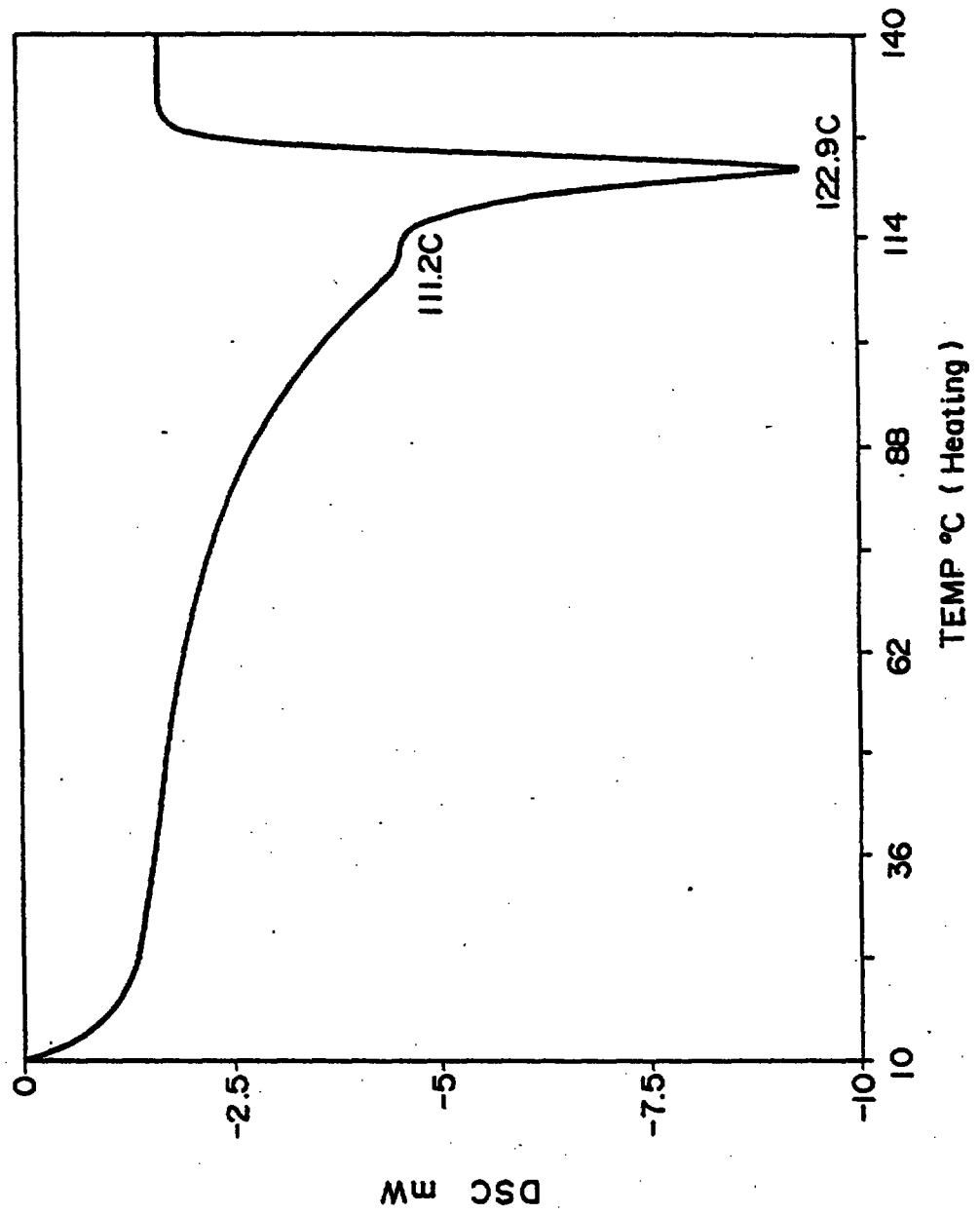
FIG. 7



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FIG. 8

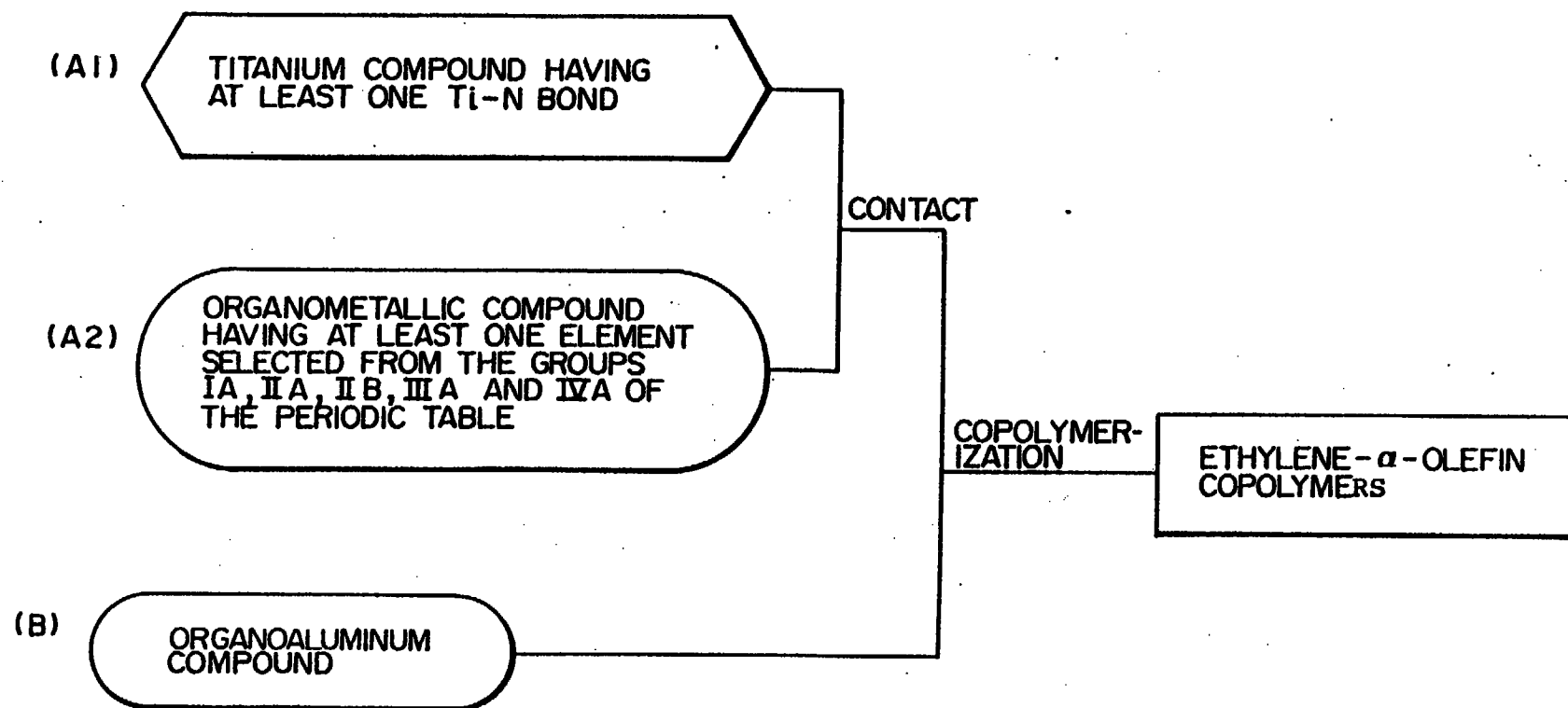


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FIG. 9

(A) REACTION PRODUCT



ABSTRACT

CATALYST FOR COPOLYMERIZING ETHYLENE WITH α -OLEFIN AND PROCESS FOR PRODUCING ETHYLENE- α -OLEFIN COPOLYMER USING THE CATALYST

A catalyst for copolymerizing ethylene with an α -olefin comprising a reaction product (A) of a titanium compound (A1) having at least one titanium-nitrogen bond with an organometallic compound (A2) having at least one element selected from the groups IA, IIA, IIB, IIIA and IVA of the periodic table and an organoaluminum compound (B), and a process for producing ethylene- α -olefin copolymers using the above catalyst. The present invention can provide a catalyst having a high activity per unit weight of transition metal and an ethylene- α -olefin copolymer having narrow composition distribution and a high molecular weight and excellent in weather resistance, color development, transparency, corrosiveness and mechanical properties.

(Figure 9)

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FIG. 9

A REACTION PRODUCT

A1

TITANIUM COMPOUND HAVING
AT LEAST ONE TI-N BOND

A2

ORGANOMETALLIC COMPOUND
HAVING AT LEAST ONE ELEMENT
SELECTED FROM THE GROUPS
IA, IIA, IIB, IIIA AND IVA OF
THE PERIODIC TABLE

B

ORGANOALUMINUM
COMPOUND

CONTACT

COPOLYMER-
IZATION

ETHYLENE- α -OLEFIN
COPOLYMERS

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system and to provide a process for producing ethylene- α -olefin copolymers by using the catalytic system with a high yield of polymer per unit weight of transition metal which copolymers have a narrow composition distribution and a high molecular weight and are excellent in weather resistance, color development, transparency, corrosiveness, and mechanical properties.

These objects have been achieved by providing a catalyst for copolymerizing ethylene with an α -olefin which comprises the reaction product (A) of a titanium compound (A1) having at least one titanium-nitrogen bond with an organomagnesium compound (A2) and an organo-aluminum compound (B) said reaction product (A) being in the form of a liquid, and a process for producing ethylene- α -olefin copolymers which uses the catalyst.

15

Fig. 1 is a diagram showing the melting behaviour of the copolymer obtained in Example 1 determined with a differential scanning calorimeter (hereinafter abbreviated as DSC).

Fig. 2 is a diagram showing the melting behaviour of the copolymer obtained in Example 3 determined with a DSC.

Fig. 3 is a diagram showing the melting behaviour of the copolymer obtained in Comparative Example 1 determined with a DSC.

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☒ Claim(s) : paged 58... to paged 60...	
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☐ Abstract : paged to paged	
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CLAIMS:

1. A catalyst for copolymerizing ethylene with an α -olefin comprising a reaction product (A) of a titanium compound (A1) having at least one titanium-nitrogen bond with an organomagnesium compound (A2) and an organo-aluminum compound (B), said reaction product (A) being in the form of a liquid.

2. The catalyst according to claim 1 wherein the titanium compound (A1) having at least one titanium-nitrogen bond is one which is represented by the formula $(R^1R^2N)_{4-(m+n)}TiX_mY_n$, wherein R^1 and R^2 each denote a hydrocarbon group having 1-30 carbon atoms and may be the same or different, X denotes a halogen, Y denotes an alkoxy group, and m and n are numbers respectively defined by the equations $0 \leq m \leq 3$ and $0 \leq n < 3$, provided that (m+n) is defined by the equation $0 \leq (m+n) \leq 3$.

3. The catalyst according to claim 1, wherein the element
15 selected for the groups IA, IIA, IIB, IIIA and IVA of the periodic table is Li, Na, K, Be, Mg, Ca, Zn, Cd, B, Al, Ga, In or Sn.

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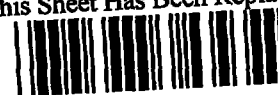


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4. The catalyst according to claim 1, wherein the organomagnesium compound is at least one organomagnesium compound selected from the group consisting of compounds represented by the following formulas:

- 5 (1) R^3R^4Mg , wherein R^3 and R^4 each denote a hydrocarbon group having 1-20 carbon atoms and may be the same or different,
(2) R^5MgZ^1 , wherein R^5 denotes a hydrocarbon group having 1-20 carbon atoms and Z^1 denotes a hydrogen atom or an alkoxy group,
(3) R^6MgX , wherein R^6 denotes a hydrocarbon group having 1 -20 10 carbon atoms and X denotes a halogen.

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5. The catalyst according to claim 1, wherein the organoaluminum compound (B) is an organoaluminum compound (B1) represented by the formula $R^{10}_aAlZ^3_{3-a}$, wherein R^{10} denotes a hydrocarbon group having 1-20 carbon atoms, Z^3 denotes a hydrogen atom and/or an alkoxy group, and a denotes a number defined by the equation $0 < a \leq 3$.

6. Use of a catalyst according to anyone of claims 1 to 5 for producing ethylene- α -olefin copolymers.

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☒ Claim(s) :	paged 48	to paged 49
☒ Drawing(s) :	1/6	to paged 46
☒ Abstract :	paged 50	to paged
DATE OF RECEIPT		1/7/99

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CATALYST FOR COPOLYMERIZING ETHYLENE WITH α -OLEFIN
 AND PROCESS FOR PRODUCING ETHYLENE- α -OLEFIN COPOLYMER
 USING THE CATALYST

1

The present invention relates to a novel Ziegler catalyst and to a process for producing ethylene- α -olefin copolymers using the catalyst. In more particular, it relates to a catalyst comprising a novel catalyst component and an organoaluminum compound and to a process for producing ethylene- α -olefin copolymers using the catalyst. In still more particular, it relates to a catalyst and to a process for producing ethylene- α -olefin copolymers which have a narrow composition distribution, have a high molecular weight, and are excellent in weather resistance, color development, transparency, corrosiveness and mechanical properties by using the catalyst.

Olefin copolymers are in a vast variety of uses, including film, laminates, electric wire covering, injection molded articles, and special molded articles. It is generally known that, to obtain products which are excellent in transparency, impact resistance, anti-blocking property in these uses, polymers which have narrow molecular weight distribution and composition distribution are preferably used. In the case of

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1 copolymers, particularly, as the content of copolymerized
α-olefin increases, the influences of molecular weight
distribution and composition distribution exerted on the
properties of the copolymer become greater. Accordingly,
5 olefin copolymers which have narrow molecular weight
distribution and composition distribution are eagerly
waited for.

Among the methods for producing olefin
copolymers, there are widely known a group of methods
10 which use so-called Ziegler-Natta catalysts, which
comprise a compound of a transition metal of the groups
IV to VI of the periodic table and an organometallic
compound of the groups I to III.

As to Ziegler-type solid catalysts, there have
15 been proposed catalysts comprising a transition metal
compound, such as titanium tetrachloride, supported on a
carrier, such as a magnesium compound (Belgian Patent
Application No. 759601, JP-B-47-46269, JP-B-47-26383, and
others), and solid catalytic systems obtained by reducing
20 a titanium compound with an organomagnesium compound,
which include a solid catalyst component comprising a
Grignard reagent and titanium tetrachloride or an
alkoxy-containing titanium halide (JP-A-46-4391,
JP-B-47-40959, JP-B-50-30102, and others), and a solid
25 catalyst component obtained by reacting a Grignard
reagent and an alkoxy-containing titanium halide and
treating the reaction product with titanium tetrachloride
(JP-B-57-24361, JP-A-56-115302, and others). These

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1 Patent 867243 give ethylene- α -olefin copolymers having a
wide composition distribution, while the methods dis-
closed in EP-0104374, JP-B-42-11646, JP-B-42-22691 and J.
of Polym. Sci. Part A-1, 241, 6 (1968) are not satis-
5 factory in the activity and copolymerizability of the
catalyst and the width of composition distribution of the
copolymer obtained.

To solve the problems described above, the
present inventors previously proposed a process for
10 producing, in copolymerization of ethylene with an α -
olefin, a copolymer having a narrow composition
distribution by using a catalytic system comprising a
titanium compound represented by the formula
 $(R^1R^2N)_4-(m+n)TiX_mY_n$, wherein R^1 and R^2 are each a
15 saturated hydrocarbon group having 8-30 carbon atoms, X
is a halogen, Y is an alkoxy group, and m and n are
respectively numbers defined by the equations $1 \leq m \leq 3$
and $0 \leq n \leq 2$, provided that (m+n) is defined by the
equation $1 \leq (m+n) \leq 3$, and an organoaluminum compound
20 (JP-A-2-77412).

The above process, however, is not fully satis-
factory in the activity of the catalyst, though it gives
copolymers having substantially improved composition
distribution.

25

In view of the above situation, the object of
the present invention is to provide a catalytic

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1 system and to provide a process for producing ethylene-
α-olefin copolymers by using the catalytic system with a
high yield of polymer per unit weight of transition metal
which copolymers have a narrow composition distribution
5 and a high molecular weight and are excellent in weather
resistance, color development, transparency, corrosive-
ness, and mechanical properties.

These objects have been achieved by providing
a catalyst for copolymerizing ethylene with
10 an α-olefin which comprises the reaction product (A) of a
titanium compound (A1) having at least one titanium-
nitrogen bond with an organomagnesium compound (A2) and
an aluminum compound (B), said reaction product (A) being
in the form of a liquid,
15 and a process for producing
ethylene-α-olefin copolymers which uses the catalyst.

Fig. 1 is a diagram showing the melting
behavior of the copolymer obtained in Example 1
20 determined with a differential scanning calorimeter
(hereinafter abbreviated as DSC).

Fig. 2 is a diagram showing the melting
behavior of the copolymer obtained in Example 3
determined with a DSC.

25 Fig. 3 is a diagram showing the melting
behavior of the copolymer obtained in Comparative Example
1 determined with a DSC.

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1 Fig. 4 is a diagram showing the melting
behavior of the copolymer obtained in Example 7 deter-
mined with a DSC.

 Fig. 5 is a diagram showing the melting
5 behavior of the copolymer obtained in Example 8 deter-
mined with a DSC.

 Fig. 6 is a flow chart to help understanding
the present invention. The flow chart merely represents
a typical example of the embodiments of the present
invention, and the present invention is in no way limited
20 thereto.

 The present invention will now be described in
detail below.

 The titanium compound (Al) used in the present
25 invention is a compound which has at least one titanium-
nitrogen bond. It may be, for example, a titanium
compound represented by the formula $(R^1R^2N)_{4-(m+n)}TiX_mY_n$,

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- 1 amino)titanium chloride, tetrakis(dimethylamino)titanium,
diethylaminotitanium trichloride, bis(diethylamino)-
titanium dichloride, tris(diethylamino)titanium chloride,
tetrakis(diethylamino)titanium, diisopropylaminotitanium
5 trichloride, bis(diisopropylamino)titanium dichloride,
tris(diisopropylamino)titanium chloride, tetrakis(diiso-
propylamino)titanium, dipropylaminotitanium trichloride,
bis(dipropylamino)titanium dichloride, tris(dipropyl-
amino)titanium chloride, tetrakis(dipropylamino)titanium,
10 diisobutylaminotitanium trichloride, bis(diisobutyl-
amino)titanium dichloride, tris(diisobutylamino)titanium
chloride, tetrakis(diisobutylamino)titanium, di-tert-
butylaminotitanium trichloride, bis(di-tert-butylamino)-
titanium dichloride, tris(di-tert-butylamino)titanium
15 chloride, tetrakis(di-tert-butylamino)titanium,
dibutylaminotitanium trichloride, bis(dibutylamino)-
titanium dichloride, tris(dibutylamino)titanium chloride,
tetrakis(dibutylamino)titanium, dihexylaminotitanium
trichloride, bis(dihexylamino)titanium dichloride,
20 tris(dihexylamino)titanium chloride, tetrakis-
(dihexylamino)titanium, dioctylaminotitanium trichloride,
bis(dioctylamino)titanium dichloride, tris(dioctyl-
amino)titanium chloride, tetrakis(dioctylamino)titanium,
didecylaminotitanium trichloride, bis(didecylamino)-
25 titanium dichloride, tris(didecylamino)titanium
chloride, tetrakis(didecylamino)titanium, dioctadecyl-
aminotitanium trichloride, bis(dioctadecylamino)titnaium
dichloride, tris(dioctadecylamino)titanium chloride,

- 14 -

- 1 tetrakis(dioctadecylamino)titanium, ethoxy(dimethyl-
amino)titanium dichloride, ethoxy(diethylamino)titanium
dichloride, ethoxy(dipropylamino)titanium dichloride,
ethoxy(diisopropylamino)titanium dichloride, ethoxy-
5 (diisobutylamino)titanium dichloride, ethoxy(di-tert-
butylamino)titanium dichloride, ethoxy(dibutylamino)-
titanium dichloride, ethoxy(dihexylamino)titanium
dichloride, ethoxy(dioctylamino)titanium dichloride,
propoxy(dimethylamino)titanium dichloride, propoxy-
10 (diethylamino)titanium dichloride, propoxy(dipropyl-
amino)titanium dichloride, propoxy(diisopropylamino)-
titanium dichloride, propoxy(diisobutylamino)titanium
dichloride, propoxy(di-tert-butylamino)titanium
dichloride, propoxy(dibutylamino)titanium dichloride,
15 propoxy(dihexylamino)titanium dichloride, propoxy-
(dioctylamino)titanium dichloride, butoxy(dimethyl-
amino)titanium dichloride, butoxy(diethylamino)titanium
dichloride, butoxy(dipropylamino)titanium dichloride,
butoxy(diisopropylamino)titanium dichloride, butoxy-
20 (diisobutylamino)titanium dichloride, butoxy(di-tert-
butylamino)titanium dichloride, butoxy(dibutylamino)-
titanium dichloride, butoxy(dihexylamino)titanium
dichloride, butoxy(dioctylamino)titanium dichloride,
hexyloxy(dioctylamino)titanium dichloride, 2-
25 ethylhexyloxy(dioctylamino)titanium dichloride,
decyloxy(dioctylamino)titanium dichloride, ethoxy-
(didecylamino)titanium dichloride, hexyloxy-
(didecylamino)titanium dichloride, 2-ethylhexyloxy-

- 1 (didecylamino)titanium dichloride, decyloxy(didecyl-
amino)titanium dichloride, ethoxy(dioctadecylamino)-
titanium dichloride, 2-ethylhexyloxy(dioctadecyl-
amino)titanium dichloride, decyloxy(dioctadecylamino)-
5 titanium dichloride, hexyloxybis(dioctylamino)titanium
chloride, 2-ethylhexyloxybis(dioctylamino)titanium
chloride, decyloxybis(dioctylamino)titanium chloride,
hexyloxybis(didecylamino)titanium chloride, 2-
ethylhexyloxybis(didecylamino)titanium chloride,
10 decyloxybis(didecylamino)titanium chloride,
hexyloxybis(dioctadecylamino)titanium chloride, 2-
ethylhexyloxybis(dioctadecylamino)titanium chloride,
decyloxybis(dioctadecylamino)titanium chloride,
methoxytris(dimethylamino)titanium, ethoxytris-
15 (dimethylamino)titanium, butoxytris(dimethylamino)-
titanium, hexyloxytris(dimethylamino)titanium, 2-
ethylhexyloxytris(dimethylamino)titanium, decyloxytris-
(dimethylamino)titanium, methoxytris(diethylamino)-
titanium, ethoxytris(diethylamino)titanium,
20 butoxytris(diethylamino)titanium, hexyloxytris-
(diethylamino)titanium, 2-ethylhexyloxytris(diethyl-
amino)titanium, decyloxytris(diethylamino)titanium,
methoxytris(dipropylamino)titanium, ethoxytris-
(dipropylamino)titanium, butoxytris(dipropylamino)-
25 titanium, hexyloxytris(dipropylamino)titanium, 2-
ethylhexyloxytris(dipropylamino)titanium, decyloxytris-
(dipropylamino)titanium, methoxytris(dibutylamino)-
titanium, ethoxytris(dibutylamino)titanium,

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- 1 butoxytris(dibutylamino)titanium, hexyloxytris(dibutyl-
amino)titanium, 2-ethylhexyloxytris(dibutylamino)-
titanium, decyloxytris(dibutylamino)titanium,
methoxytris(dihexylamino)titanium, ethoxytris(dihexyl-
5 amino)titanium, butoxytris(dihexylamino)titanium,
hexyloxytris(dihexylamino)titanium, 2-ethylhexyloxy-
tris(dihexylamino)titanium, decyloxytris(dihexylamino)-
titanium, methoxytris(dioctylamino)titanium,
ethoxytris(dioctylamino)titanium, butoxytris(dioctyl-
10 amino)titanium, hexyloxytris(dioctylamino)titanium, 2-
ethylhexyloxytris(dioctylamino)titanium, decyloxytris-
(dioctylamino)titanium, methoxytris(didecylamino)-
titanium, ethoxytris(didecylamino)titanium, butoxytris-
(didecylamino)titanium, hexyloxytris(didecylamino)-
15 titanium, 2-ethylhexyloxytris(didecylamino)titanium,
decyloxytris(didecylamino)titanium, methoxytris-
(dioctadecylamino)titanium, ethoxytris(dioctadecyl-
amino)titanium, butoxytris(dioctadecylamino)titanium,
hexyloxytris(dioctadecylamino)titanium, 2-ethylhexyloxy-
20 tris(dioctadecylamino)titanium, and decyloxytris-
(dioctadecylamino)titanium.

Among such titanium compounds, when R^1 and R^2
are each an aliphatic hydrocarbon group, particularly
those wherein the number of carbon atoms is 8-30 are
25 preferred. Further, even when the number of carbon atoms
is less than 8, those compounds wherein m is 0 or 2 are
more preferred because they give copolymers having a
narrower composition distribution. Specific examples of

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- 1 such compounds include bis(dimethylamino)titanium
dichloride, tetrakis(dimethylamino)titanium,
bis(diethylamino)titanium dichloride, tetrakis-
(diethylamino)titanium, bis(diisopropylamino)titanium
5 dichloride, tetrakis(diisopropylamino)titanium,
bis(dipropylamino)titanium dichloride, tetrakis(dipropyl-
amino)titanium, bis(diisobutylamino)titanium dichloride,
tetrakis(diisobutylamino)titanium, bis(di-tert-
butylamino)titanium dichloride, tetrakis(di-tert-
10 butylamino)titanium, bis(dibutylamino)titanium
dichloride, tetrakis(dibutylamino)titanium, bis(dihexyl-
amino)titanium dichloride, tetrakis(dihexylamino)-
titanium, dioctylaminotitanium trichloride, bis-
(dioctylamino)titanium dichloride, tris(dioctyl-
15 amino)titanium chloride, tetrakis(dioctylamino)titanium,
didecylaminotitanium trichloride, bis(didecylamino)-
titanium dichloride, tris(didecylamino)titanium chloride,
tetrakis(didecylamino)titanium, dioctadecylaminotitanium
trichloride, bis(dioctadecylamino)titanium dichloride,
20 tris(dioctadecylamino)titanium chloride, tetrakis-
(dioctadecylamino)titanium, ethoxy(dimethylamino)titanium
dichloride, ethoxy(diethylamino)titanium dichloride,
ethoxy(dipropylamino)titanium dichloride, ethoxy(diiso-
propylamino)titanium dichloride, ethoxy(diisobutylamino)-
25 titanium dichloride, ethoxy(di-tert-butylamino)titanium
dichloride, ethoxy(dibutylamino)titanium dichloride,
ethoxy(dihexylamino)titanium dichloride, ethoxy-
(dioctylamino)titanium dichloride, propoxy(dimethyl-

- 1 amino)titanium dichloride, propoxy(diethylamino)titanium
dichloride, propoxy(dipropylamino)titanium dichloride,
propoxy(diisopropylamino)titanium dichloride, propoxy-
(diisobutylamino)titanium dichloride, propoxy(di-tert-
5 butylamino)titanium dichloride, propoxy(dibutylamino)-
titanium dichloride, propoxy(dihexylamino)titanium
dichloride, propoxy(dioctylamino)titanium dichloride,
butoxy(dimethylamino)titanium dichloride, butoxy-
(diethylamino)titanium dichloride, butoxy(dipropyl-
10 amino)titanium dichloride, butoxy(diisopropylamino)-
titanium dichloride, butoxy(diisobutylamino)titanium
dichloride, butoxy(di-tert-butylamino)titanium
dichloride, butoxy(dibutylamino)titanium dichloride,
butoxy(dihexylamino)titanium dichloride, butoxy-
15 (dioctylamino)titanium dichloride, hexyloxy(dioctyl-
amino)titanium dichloride, 2-ethylhexyloxy(dioctyl-
amino)titanium dichloride, decyloxy(dioctylamino)titanium
dichloride, ethoxy(didecylamino)titanium dichloride,
hexyloxy(didecylamino)titanium dichloride, 2-
20 ethylhexyloxy(didecylamino)titanium dichloride,
decyloxy(didecylamino)titanium dichloride, ethoxy-
(dioctadecylamino)titanium dichloride, 2-ethylhexyloxy-
(dioctadecylamino)titanium dichloride, decyloxy(diocta-
decylamino)titanium dichloride, hexyloxybis(dioctyl-
25 amino)titanium chloride, 2-ethylhexyloxybis(dioctyl-
amino)titanium chloride, decyloxybis(dioctyl-
amino)titanium chloride, hexyloxybis(didecylamino)-
titanium chloride, 2-ethylhexyloxybis(didecylamino)-

- 1 hexyloxytris(dihexylamino)titanium, 2-ethylhexyloxytris-
(dihexylamino)titanium, decyloxytris(dihexylamino)-
titanium, methoxytris(dioctylamino)titanium, ethoxytris-
(dioctylamino)titanium, butoxytris(dioctylamino)titanium,
5 hexyloxytris(dioctylamino)titanium, 2-ethylhexyloxytris-
(dioctylamino)titanium, decyloxytris(dioctylamino)-
titanium, methoxytris(didecylamino)titanium, ethoxytris-
(didecylamino)titanium, butoxytris(didecylamino)titanium,
hexyloxytris(didecylamino)titanium, 2-ethylhexyloxy-
10 tris(didecylamino)titanium, decyloxytris(didecylamino)-
titanium, methoxytris(dioctadecylamino)titanium,
ethoxytris(dioctadecylamino)titanium, butoxytris-
(dioctadecylamino)titanium, hexyloxytris(dioctadecyl-
amino)titanium, 2-ethylhexyloxytris(dioctadecyl-
15 amino)titanium, and decyloxytris(dioctadecylamino)-
titanium.

Such titanium compounds (Al) may be
synthesized, for example, by using the methods described
in JP-B-41-5397; JP-B-42-11646; H. Burger et al., J. of
20 Organomet. Chem., 108 (1976), 69-84; H. Burger et al., J.
of Organomet. Chem., 20 (1969), 129-139; and H. Burger,
Z. Anorg. Allg. Chem., 365, 243-254 (1991).

The titanium compounds may be synthesized,
according to the aforesaid methods, for example, by
25 reacting (i) a secondary amine represented by the formula
 $R^{11}R^{12}NH$, wherein R^{11} and R^{12} each denote a hydrocarbon
group having 1-30 carbon atoms and may be the same or
different, with (ii) an alkylalkali metal represented by

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- 1 the formula $R^{13}M$, wherein R^{13} denotes a hydrocarbon group
having 1-30 carbon atoms and M denotes an alkali metal
such as Li and K, and then reacting the resulting alkali
metal amide with a titanium tetrahalide represented by
5 the formula TiX_4 , wherein X denotes a halogen, such as
chlorine, bromine, or iodine, preferably chlorine.

In the above synthesis, two or more alkali
metal amides may be used simultaneously in combination.

- 1 amylbenzylmagnesium, amylvinylmagnesium, amyl-2-
propenylmagnesium, amyl-2-butenylmagnesium, amyl-
(trimethylsilylmethyl)magnesium, neopentylhexylmagnesium,
neopentylcyclohexylmagnesium, neopentylphenylmagnesium,
5 neopentylbenzylmagnesium, neopentylvinylmagnesium,
neopentyl-2-propenylmagnesium, neopentyl-2-butenyl-
magnesium, neopentyl(trimethylsilylmethyl)magnesium,
hexylcyclohexylmagnesium, hexylphenylmagnesium,
hexylbenzylmagnesium, hexylvinylmagnesium, hexyl-2-
10 propenylmagnesium, hexyl-2-butenylmagnesium, hexyl-
(trimethylsilylmethyl)magnesium, cyclohexylphenyl-
magnesium, cyclohexylbenzylmagnesium, cyclohexylvinyl-
magnesium, cyclohexyl-2-propenylmagnesium, cyclohexyl-
2-butenylmagnesium, cyclohexyl(trimethylsilylmethyl)-
15 magnesium, phenylbenzylmagnesium, phenylvinylmagnesium,
phenyl-2-propenylmagnesium, phenyl-2-butenylmagnesium,
phenyl(trimethylsilylmethyl)magnesium, benzylvinyl-
magnesium, benzyl-2-propenylmagnesium, benzyl-2-
butenylmagnesium, benzyl(trimethylsilylmethyl)magnesium,
20 vinyl-2-propenylmagnesium, vinyl-2-butenylmagnesium, and
vinyl(trimethylsilylmethyl)magnesium.

- Examples of the compounds represented by the
formula R^5MgZ^1 include ethylmagnesium hydride,
propylmagnesium hydride, isopropylmagnesium hydride,
25 butylmagnesium hydride, sec-butylmagnesium hydride,
tert-butylmagnesium hydride, phenylmagnesium hydride,
ethylmagnesium methoxide, ethylmagnesium ethoxide,
ethylmagnesium propoxide, ethylmagnesium butoxide,

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- 1 ethylmagnesium phenoxide, propylmagnesium methoxide,
propylmagnesium ethoxide, propylmagnesium propoxide,
propylmagnesium butoxide, propylmagnesium phenoxide,
isopropylmagnesium methoxide, isopropylmagnesium
5 ethoxide, isopropylmagnesium propoxide, isopropyl-
magnesium butoxide, isopropylmagnesium phenoxide,
butylmagnesium methoxide, butylmagnesium ethoxide,
butylmagnesium propoxide, butylmagnesium butoxide,
butylmagnesium phenoxide, sec-butylmagnesium methoxide,
10 sec-butylmagnesium ethoxide, sec-butylmagnesium
propoxide, sec-butylmagnesium butoxide, sec-butyl-
magnesium phenoxide, tert-butylmagnesium methoxide,
tert-butylmagnesium ethoxide, tert-butylmagnesium
propoxide, tert-butylmagnesium butoxide, tert-
15 butylmagnesium phenoxide, phenylmagnesium methoxide,
phenylmagnesium ethoxide, phenylmagnesium propoxide,
phenylmagnesium butoxide and phenylmagnesium phenoxide.

Examples of the compounds represented by the
formula R^6MgX include methylmagnesium chloride,

- 20 ethylmagnesium chloride, ethylmagnesium bromide,
ethylmagnesium iodide, propylmagnesium chloride,
propylmagnesium bromide, butylmagnesium chloride,
butylmagnesium bromide, sec-butylmagnesium chloride,
sec-butylmagnesium bromide, tert-butylmagnesium chloride,
25 tert-butylmagnesium bromide, amylmagnesium chloride,
isoamylmagnesium chloride, vinylmagnesium bromide,
vinylmagnesium chloride, 1-propenylmagnesium bromide, 1-
propenylmagnesium chloride, 2-propenylmagnesium bromide,

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- 1 2-propenylmagnesium chloride, phenylmagnesium chloride,
phenylmagnesium bromide, benzylmagnesium chloride, and
benzylmagnesium bromide.

From the viewpoint of the composition distribu-
5 tion of the copolymer formed, the organomagnesium
compounds are preferably those which are represented by
the formula R^3R^4Mg . Among them, those wherein R^3 and R^4
are each an aliphatic hydrocarbon group are more
preferred. Specific examples of such organomagnesium
10 compounds include dimethylmagnesium, diethylmagnesium,
dipropylmagnesium, diisopropylmagnesium, dibutyl-
magnesium, diisobutylmagnesium, di-sec-butylmagnesium,
di-tert-butylmagnesium, diamylmagnesium, dineopentyl-
magnesium, dihexylmagnesium, dicyclohexylmagnesium,
15 methylethylmagnesium, methylpropylmagnesium,
methylisopropylmagnesium, methylbutylmagnesium,
methylibutylmagnesium, methyl-sec-butylmagnesium,
methyl-tert-butylmagnesium, methylamylmagnesium,
methylneopentylmagnesium, methylhexylmagnesium,
20 methylcyclohexylmagnesium, ethylpropylmagnesium,
ethylisopropylmagnesium, ethylbutylmagnesium, ethyl-
isobutylmagnesium, ethyl-sec-butylmagnesium, ethyl-tert-
butylmagnesium, ethylamylmagnesium, ethylneopentyl-
magnesium, ethylhexylmagnesium, ethylcyclohexylmagnesium,
25 propylisopropylmagnesium, propylbutylmagnesium,
propylisobutylmagnesium, propyl-sec-butylmagnesium,
propyl-tert-butylmagnesium, propylamylmagnesium,
propylneopentylmagnesium, propylhexylmagnesium,

- 1 propylcyclohexylmagnesium, isopropylbutylmagnesium,
isopropylisobutylmagnesium, isopropyl-sec-butylmagnesium,
isopropyl-tert-butylmagnesium, isopropylamylmagnesium,
isopropylneopentylmagnesium, isopropylhexylmagnesium,
5 isopropylcyclohexylmagnesium, butylisobutylmagnesium;
butyl-sec-butylmagnesium, butyl-tert-butylmagnesium,
butylamylmagnesium, butylneopentylmagnesium, butylhexyl-
magnesium, butylcyclohexylmagnesium, isobutyl-sec-
butylmagnesium, isobutyl-tert-butylmagnesium,
10 isobutylamylmagnesium, isobutylneopentylmagnesium,
isobutylhexylmagnesium, isobutylcyclohexylmagnesium,
sec-butyl-tert-butylmagnesium, sec-butylamylmagnesium,
sec-butylneopentylmagnesium, sec-butylhexylmagnesium,
sec-butylcyclohexylmagnesium, tert-butylamylmagnesium,
15 tert-butylneopentylmagnesium, tert-butylhexylmagnesium,
tert-butylcyclohexylmagnesium, amylneopentylmagnesium,
amylhexylmagnesium, amylcyclohexylmagnesium, neopentyl-
hexylmagnesium, neopentylcyclohexylmagnesium, and
hexylcyclohexylmagnesium.

- 20 In place of the aforesaid organomagnesium
compounds, hydrocarbon soluble complexes of the
organomagnesium compounds with organometallic compounds
may be used. The organometallic compounds may be, for
example, organic compounds of Li, Be, B, Al or Zn.
25 Further, the present invention is not limited to the
aforesaid compounds.

The organoaluminum compounds (B) used as one component of the catalyst in the present invention may be those known in the art. The organoaluminum compounds (B) may be, for example, organoaluminum compounds (B1) represented by the formula $R^{10}_aAlZ^3_{3-a}$, and chain-like or cyclic aluminoxanes (B2) having the structure shown by the formula $-[A_\ell(R^{11})-O]_\ell-$. Preferred among the organoaluminum compounds (B) are organoaluminum compounds (B1) represented by the formula $R^{10}_aAlZ^3_{3-a}$. In the above formulas, R^{10} and R^{11} are each a hydrocarbon group having 1-20 carbon atoms, preferably 1-10 carbon atoms,

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- 1 z^3 denotes a hydrogen atom and/or an alkoxy group, a is a number defined by the equation $0 < a \leq 3$, and l is an integer of 1 or more, preferably 2-30.

Specific examples of the organoaluminum

- 5 compounds (B1) represented by the formula $R^{10}_a Al z^3_{3-a}$ include trialkylaluminums, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, and tridecylaluminum, dialkylaluminum hydrides, such as
10 dimethylaluminum hydride, diethylaluminum hydride, dipropylaluminum hydride, diisobutylaluminum hydride, dihexylaluminum hydride, dioctylaluminum hydride, and didecylaluminum hydride, alkoxyaluminum hydrides, such as methoxymethylaluminum hydride, methoxyethylaluminum
15 hydride, methoxyisobutylaluminum hydride, ethoxyhexylaluminum hydride, ethoxyoctylaluminum hydride, and ethoxydecylaluminum hydride, and alkylaluminum alkoxides, such as dimethylaluminum methoxide, methylaluminum dimethoxide, diethylaluminum methoxide, ethylaluminum
20 dimethoxide, diisobutylaluminum methoxide, isobutylaluminum dimethoxide, dihexylaluminum methoxide, hexylaluminum dimethoxide, dimethylaluminum ethoxide, methylaluminum diethoxide, diethylaluminum ethoxide, ethylaluminum diethoxide, diisobutylaluminum ethoxide,
25 and isobutylaluminum diethoxide.

Preferred of such compounds from the viewpoint of catalytic activity are trialkylaluminums, which are compounds of the formula wherein a is 3, such as

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1 trimethylaluminum, triethylaluminum, tripropylaluminum,
triisobutylaluminum, trihexylaluminum, and the like.
However, the present invention is not limited to the
above-mentioned compounds.

5 Specific examples of aluminoxanes (B2)
represented by the formula $-[Al(R^{11})-O]_x-$ include
tetramethyldialuminoxane, tetraethyldialuminoxane,
tetrabutylaluminoxane, tetrahexyldialuminoxane,
methylaluminoxane, ethylaluminoxane, butylaluminoxane,
10 hexylaluminoxane, and the like. The present invention,
however, is not limited to the above-mentioned compounds.

The component (B) may be used in a wide range
such as usually 0.01-10,000 moles relative to 1 mole of
titanium atom of the component (A), but it is preferably
15 used in the range of 0.05-500 moles, more preferably
0.1-50 moles, relative to 1 mole of titanium atom.

Next, the synthesis of the reaction product (A)
in the present invention is described below.

The reaction product (A), namely one of the
20 catalyst components in the present invention, can be
prepared by reacting a titanium compound (A1) with an
organometallic compound (A2). When the reaction product
thus obtained contains a solid,

the
25 solid is removed by filtration and the resulting liquid
alone is used for polymerization. The use of the solid
is not preferable because the solid formed has a
very low catalytic activity as compared with the liquid

1 component and further gives copolymers having a wide
composition distribution.

The reaction of the titanium compound (A1) with
the organometallic compound (A2) may be effected either
5 by adding the organometallic compound (A2) to the
titanium compound (A1) or by adding the titanium compound
(A1) to the organometallic compound (A2).

The reaction temperature is usually in the
range of -50 to 230°C, preferably 0 to 200°C. The
10 reaction time is not particularly restricted, but usually
1 minutes to 2 hours.

The amount of the organometallic compound (A2)
used is, in terms of the atomic ratio of the metal in the
organometallic compound (A2) to the titanium in the
15 titanium compound (A1), in the range of usually 0.01-100,
preferably 0.05-50, more preferably 0.1-10.

The catalyst components and the catalyst
according to the present invention are used for producing
ethylene- α -olefin copolymers. Said copolymers herein
20 refer to copolymers formed from ethylene and one or more
 α -olefin.

Specific examples of the α -olefin include α -
olefins having 3-30 carbon atoms, such as propylene,
butene-1, pentene-1, hexene-1, 4-methylpentene-1,
25 octene-1, decene-1, octadecene-1, and eicosene-1.

Further, dienes may also be copolymerized in
order to improve the vulcanizability of the copolymer.
Specific examples of such dienes include 1,3-butadiene,

1 dicyclopentadiene, tricyclopentadiene, 5-methyl-2,5-
norbornadiene, 5-methylene-2-norbornene, 5-ethyldiene-2-
norbornene, 5-isopropenyl-2-norbornene, 5-(2'-butenyl)-
2-norbornene, 1,5,9-cyclododecatriene, 6-methyl-4,7,8,9-
5 tetrahydroindene, trans-1,2-divinylcyclobutane, 1,4-
hexadiene, 4-methyl-1,4-hexadiene, 1,3-hexadiene, 1,6-
octadiene, and 6-methyl-1,5-heptadiene. The present
invention, however, is not to be limited to the above
compounds.

10 The copolymer obtained according to the present
invention can have a density in the range of 0.85-0.95
g/cm³, but preferably has a density in the range of
0.88-0.95 g/cm³, more preferably 0.90-0.95 g/cm³.

An example of the process for producing
15 ethylene- α -olefin copolymers using the catalyst
components or the catalyst according to the present
invention is described below.

The method for feeding the respective catalyst
components to the polymerization vessel is subject to no
20 particular restriction except that they should be fed in
an inert gas, such as nitrogen or argon, and in the
absence of moisture. The catalyst components (A) and (B)
may be either fed each individually or fed after having
been made to contact with each other in advance.

25 The polymerization temperature may be usually
in the range of -30 to 300°C, but is preferably 0 to
280°C, more preferably 20 to 250°C.

The polymerization pressure is not particularly

1 restricted, but preferably about 3-1500 atm from the
viewpoint of industrial practicality and economical
efficiency.

The polymerization can be conducted either
5 continuously or batchwise. It may be slurry or solution
polymerization which use an inert hydrocarbon solvent,
such as propane, butane, pentane, hexane, and octane, or
liquid phase or gas phase polymerization which use no
solvent.

10 Further, a chain transfer agent, such as
hydrogen, may be added to the polymerization system in
order to control the molecular weight of the copolymer of
the present invention.

According to the present invention, a catalyst
15 having a high catalytic activity per unit weight of
transition metal is obtained, whereby productivity can
be improved and further the production of ethylene- α -
olefin copolymers having a high molecular weight and
narrow composition distribution becomes possible; thus,
20 ethylene- α -olefin copolymers excellent in weather
resistance, color development, transparency, corrosive-
ness, and mechanical properties can be provided.

The present invention will be described further
in detail below with reference to Examples and
25 Comparative Examples.

The polymer properties described in Examples
were determined by the following methods.

The α -olefin content was determined from the

- 1 characteristic absorptions of ethylene and α -olefin
measured by using an infrared spectrophotometer (JASCO-
302, mfd. by NIPPON BUNKO KOGYO CO.).

The intrinsic viscosity $[\eta]$ was determined by
5 using an Ubbelohde's viscometer in tetralin solution at
135°C.

As the measure for representing composition
distribution, an average melting point $\langle T_m \rangle$ defined by
the following equation was determined by using a
10 differential scanning calorimeter (DSC). The smaller
 $\langle T_m \rangle$ value indicates the narrower composition distribu-
tion.

$$\langle T_m \rangle = \frac{\sum (H_i \times t_i)}{\sum H_i}$$

wherein $50^\circ\text{C} < t_i < 120^\circ\text{C}$, and H_i denotes the melting
energy (w/g) at temperature t_i .

15 Example 1

(1) Synthesis of reaction product (A)

Synthesis of titanium compound (A1):

A 300-ml flask equipped with a stirrer,
dropping funnel and thermometer was purged with argon
20 gas, and 18.1 ml (60 mmols) of dioctylamine and 150 ml of
hexane were charged therein.

Then, 38.7 ml (60 mmols) of n-butyllithium
diluted with hexane was added dropwise from the dropping

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- 1 funnel over a period of 30 minutes with stirring while
keeping the temperature of the solution in the flask at
5°C. After completion of the addition, the reaction was
further conducted at 5°C for 2 hours and at 30°C for 2
5 hours.

Then, 2.2 ml (20 mmols) of TiCl_4 diluted with
hexane was added dropwise from the dropping funnel to the
liquid mixture obtained by the above reaction over a
period of 30 minutes while keeping the temperature of the
10 liquid mixture at 5°C. After completion of the addition,
the reaction was further continued at 5°C for 1 hour and
at 30°C for 2 hours, to obtain 20 mmols (as 100% yield)
of a titanium compound (A-1) represented by the compo-
sition formula $[(\text{C}_8\text{H}_{17})_2\text{N}]_3\text{TiCl}$.

- 15 Reaction of titanium compound (A1) with organometallic
compound (A2):

To the reaction product obtained above was
added 30 ml (19.8 mmols) of butylethylmagnesium
(hereinafter abbreviated as BEM) (mfd. by Tosoh-Akzo Co.)
20 diluted with heptane, and the resulting mixture was
allowed to react for 1 hour while keeping the temperature
at 30°C, to obtain 20 mmols of a reaction product (A)
(hereinafter called "component (A)"). (catalyst
concentration: 0.077 mmol Ti/ml).

- 25 (2) Polymerization of ethylene

An autoclave of 400-ml inner volume equipped

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with a stirrer and a thermometer was dried under vacuum and purged with argon gas. Then, 100 ml of toluene as a solvent and 800 mmols of hexene-1 as an α -olefin were charged therein, and the reactor was heated up to 180°C. Thereafter, ethylene was fed into the reactor while adjusting the ethylene pressure to 25 kg/cm² (1 kg/cm²= 0.981 bar). After the reaction system had become stable, 0.1 mmol of triethylaluminum (hereinafter abbreviated as TEA) was fed as the organoaluminum compound (B) and succeedingly 0.063 mmol of the component (A) synthesized in (1) above was fed into the reactor. Then polymerization was conducted for 2 minutes while controlling the temperature at 180°C. As the result of the polymerization, 47,000 g of copolymer was obtained per 1 mol of transition metal (activity: 47,000 g-copolymer/mol. M). The results are shown in Table 1. The melting behavior of the copolymer obtained was determined with a DSC and the resulting diagram is shown in Fig. 1. In Fig. 1, the numbers of the abscissa indicate the temperature (°C) and those on the ordinate indicate the melting energy (mW). In Fig. 1, as the melting peak is recognized at the lower temperature side, the composition distribution tends to be the narrower. The composition distribution of the copolymer obtained was shown to be very narrow.

Example 2

A reaction product was synthesized in the same manner as in the synthesis of the reaction product (A) of

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- 1 Example 1(1) except that dihexylmangesium (abbreviated as
DHM) (made by Tosoh-Akzo Co.) was used in place of BEM,
and then ethylene was polymerized in the same manner as
in Example 1 except that the reaction product obtained
5 above was used in place of the reaction product (A) of
Example 1. The results are shown in Table 1. A polymer
having a narrow composition distribution was obtained as
in Example 1.

Example 3

10 Polymerization of ethylene

- An autoclave of 400-ml inner volume equipped
with a stirrer and a thermometer was dried under vacuum
and purged with argon gas. Then, 82 g of butane as a
solvent and 321 mmols of butene-1 as an α -olefin were
15 charged therein, and the reactor was heated up to 70°C.
Thereafter, hydrogen and ethylene were fed into the
reactor while adjusting the hydrogen pressure to 1.0
kg/cm² and the ethylene pressure to 6.0 kg/cm². After
the reaction system had become stable, 0.25 mmol of TEA
20 was fed as the organoaluminum compound (B), and
succeedingly 0.16 mmol of the component (A) synthesized
in Example 1(1) was fed into the reactor. Then,
polymerization was conducted for 60 minutes while
controlling the temperature at 70°C. The results are
25 shown in Table 1. A polymer having a narrow composition
distribution was obtained as in Example 1 (see Fig. 2).

1 Comparative Example 1

Ethylene was polymerized in the same manner as in Example 3 except that 0.16 mmol of a titanium compound (A1) represented by the composition formula

5 $[(C_8H_{17})_2N]_3TiCl$ was used in the polymerization in place of the component (A). The results are shown in Table 1. The results of polymerization showed that the catalytic activity was low and the polymer obtained had a wide composition distribution (see Fig. 3).

10 Example 4

(1) Synthesis of reaction product (A)

Synthesis of titanium compound (A1):

A 300-ml flask equipped with a stirrer, dropping funnel and thermometer was purged with argon
15 gas, and then 6.3 ml (60 mmols) of diethylamine and 150 ml of hexane were charged therein.

Then, 38.7 ml (60 mmols) of n-butyllithium diluted with hexane was added dropwise from the dropping funnel over a period of 30 minutes while keeping the
20 temperature of the solution in the flask at 5°C. After completion of the addition, the reaction was further conducted at 5°C for 2 hours and at 30°C for 2 hours.

Subsequently, 3.3 ml (30 mmols) of $TiCl_4$ diluted with hexane was added dropwise from the dropping
25 funnel to the liquid mixture obtained by the above reaction over a period of 30 minutes while keeping the temperature at 5°C. After completion of the addition,

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1 the reaction was further conducted at 5°C for 1 hour and
at 30°C for 2 hours, to obtain 30 mmols (as 100% yield)
of a titanium compound (A1) represented by the composi-
tion formula $[(C_2H_5)_2N]_2TiCl_2$.

5 Reaction of titanium compound (A1) with organomagnesium
compound (A2):

To the reaction product obtained above was
added 45.5 ml (30 mmols) of butylethylmagnesium (BEM)
(mfd. by Tosoh-Akzo Co.) diluted with heptane, and the
10 resulting mixture was allowed to react for 1 hour while
keeping the temperature at 30°C, to obtain 21.2 mmols of
a reaction product (A) (catalyst concentration: 0.112
mmol Ti/ml).

(2) Polymerization of ethylene

15 Polymerization was conducted in the same manner
as in Example 1(2) except that 0.063 mmol of the
component (A) synthesized in (1) above was used as the
reaction product (A) and 0.1 mmol of triisobutylaluminum
(abbreviated as TIBA) was used as the organoaluminum
20 compound (B). The results are shown in Table 1. A
polymer having a narrow composition distribution was
obtained as in Example 1.

Comparative Example 2

Polymerization was conducted in the same manner
25 as in Example 4 except that 0.063 mmol of a titanium

1 compound represented by the composition formula
[(C₂H₅)₂N]₂TiCl₂ was added in place of the component (A)
used in ethylene polymerization of Example 4(2). The
results are shown in Table 1. The result of polymeri-
5 zation showed a very low activity of the catalyst.

Example 5

Polymerization was conducted in the same manner
as in Example 1 except that 0.1 mmol of trihexylaluminum
(abbreviated as THA) was added as the organoaluminum
10 compound in place of TEA used in ethylene polymerization
of Example 1(2). The results of polymerization are shown
in Table 1. A polymer having also a narrow composition
distribution was obtained as in Example 1.

Example 6

15 A reaction product was prepared in the same
manner as in Example 3 except that MAGALA 7.5E (a trade
name, composition formula: 7.5(n-C₄H₉)₂Mg·(C₂H₅)Al, mfd.
by Tosoh-Akzo Co.) was used in place of BEM used in the
synthesis of the reaction product (A) of Example 1(1),
20 and then ethylene was polymerized in the same manner as
in Example 3 except that the reaction product prepared
above was used. The results are shown in Table 1. The
polymerization yielded a polymer having a narrow
composition distribution as in Example 3.

Table 1

	Reaction product (A)		Organo-aluminum compound (B)	Polymerization temp. (°C)	Activity $\left(\frac{\text{g-Copolymer}}{\text{mol. M}} \right)$	*1) Comonomer content (wt.%)	[η]	<Tm> (°C)
	Titanium compound	*2) Organo-magnesium compound						
Example 1	$[(C_8H_{17})_2N]_3TiCl$	BEM	TEA	180	47000	10.4	0.55	98.4
Example 2	"	DHM	"	"	23000	9.2	0.63	98.5
Example 3	"	BEM	"	70	68000	10.0	1.53	94.4
Comp. Example 1	"	—	"	"	9200	7.6	2.75	103.8
Example 4	$[(C_2H_5)_2N]_2TiCl_2$	BEM	TIBA	180	6300	6.6	0.66	98.7
Comp. Example 2	"	—	"	"	940	—	—	—
Example 5	$[(C_8H_{17})_2N]_3TiCl$	BEM	THA	"	43000	10.9	0.60	97.9
Example 6	"	7.5E	TEA	70	36000	8.8	1.51	99.6

Note: *1) Comonomer is hexene-1, except for butene-1 in Examples 3 and 6 and Comparative Example 1.

*2) BEM: $(n-C_4H_9)Mg(C_2H_5)$ DHM: $(n-C_6H_{13})_2Mg$ 7.5E: $7.5(n-C_4H_9)_2Mg \cdot (C_2H_5)_3Al$
 TEA: $(C_2H_5)_3Al$ THA: $(n-C_6H_{13})_3Al$ TIBA: $[(CH_3)_2CHCH_2]_3Al$

1 Example 7

(1) Synthesis of reaction product (A)

A reaction product (A) was synthesized in the same manner as in Example 1 except that 12.0 ml of a 1.67
5 mol/l hexane solution of n-butyllithium was used in place of BEM diluted with heptane used in the synthesis of the reaction product (A) of Example 1(1), to obtain 20 mmols of the reaction product (A) (catalyst concentration: 0.087 mmolTi/ml).

10 (2) Copolymerization of ethylene with butene-1

An autoclave of 3000-ml inner volume equipped with a stirrer and a thermometer was dried under vacuum and purged with argon gas. Then, hydrogen to a pressure of 300 mmHg, 765 g of butane as a solvent and 140 g of
15 butene-1 as an α -olefin were charged into the reactor, and the reactor was heated up to 70°C. Thereafter, ethylene was fed to the reactor while adjusting the ethylene pressure to 6 kg/cm². After the reaction system had become stable, 1.6 mmols of triethylaluminum (TEA)
20 was fed as the organoaluminum compound (B), succeedingly 0.39 mmol of the component (A) synthesized in (1) above was fed into the reactor, and polymerization was conducted for 2 hours while controlling the temperature at 70°C. As the result of the polymerization, 30.0 g of
25 a copolymer was obtained (activity: 76,900 g-copolymer/mol·Ti·hr). The results are shown in Table 2. The melt index of the copolymer obtained was determined according

1 to JIS K-6760 at 190°C. The melting behavior of the
copolymer was determined with a DSC and the resulting
diagram is shown in Fig. 4. In Fig. 4, the numbers on
the abscissa indicate the temperature (°C), and those on
5 the ordinate indicate the melting energy. In Fig. 4, as
the melting peak is recognized at the lower temperature
side, the composition distribution tends to be the
narrower. The composition distribution of the copolymer
obtained was shown to be very narrow.

10 Example 8

Copolymerization of ethylene with butene-1 was
conducted in the same manner as in Example 7 except that
20 mmols of sec-butyllithium was used in place of n-BuLi
in the synthesis of the component (A), and the component
15 (A) thus obtained was used in the copolymerization. As
the result, 21.0 g of a copolymer was obtained (activity:
53,900). The results thus obtained are shown in Table 2
and Fig. 5.

Table 2

	Reaction product (A)		Organo- aluminum compound (B)	Activity g-polymer mol·Ti·hr	Comonomer content (wt. %)	MI	<T _m > (°C)
	Titanium compound	Organo- magnesium compound					
Example 7	$[(C_8H_{17})_2N]_3TiCl$	n-BuLi	TEA	76,900	8.6	5.8	95.1
Example 8	$[(C_8H_{17})_2N]_3TiCl$	sec-BuLi	TEA	53,900	7.9	4.9	95.6

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Claim:

1. A catalyst for copolymerizing ethylene with an α -olefin comprising a reaction product (A) of a titanium compound (A1) having at least one titanium-nitrogen bond with an organomagnesium compound (A2) and an organo-aluminum compound (B), said reaction product (A) being in the form of a liquid.

2. The catalyst according to claim 1 wherein the titanium compound (A1) having at least one titanium-nitrogen bond is one which is represented by the formula $(R^1R^2N)_{4-(m+n)}TiX_mY_n$, wherein R^1 and R^2 each denote a hydrocarbon group having 1-30 carbon atoms and may be the same or different, X denotes a halogen, Y denotes an alkoxy group, and m and n are numbers respectively defined by the equations $0 \leq m \leq 3$ and $0 \leq n < 3$, provided that (m+n) is defined by the equation $0 \leq (m+n) \leq 3$.

3. The catalyst according to claim 1, wherein the organomagnesium compound is at least one organomagnesium compound selected from the group consisting of compounds represented by the following formulas:

(1) R^3R^4Mg , wherein R^3 and R^4 each denote a hydrocarbon group having 1-20 carbon atoms and may be the same or different,

(2) R^5MgZ^1 , wherein R^5 denotes a hydrocarbon group having 1-20 carbon atoms and Z^1 denotes a hydrogen atom or an alkoxy group,

(3) R^6MgX , wherein R^6 denotes a hydrocarbon group



having 1-20 carbon atoms and X denotes a halogen.

4. The catalyst according to claim 1, wherein the organoaluminum compound (B) is an organoaluminum compound (B1) represented by the formula $R^{10}_aAlZ^{3}_{3-a}$, wherein R^{10} denotes a hydrocarbon group having 1-20 carbon atoms, Z^3 denotes a hydrogen atom and/or an alkoxy group, and a denotes a number defined by the equation $0 < a \leq 3$.
5. Use of a catalyst according to anyone of claims 1 to 4 for producing ethylene- α -olefin copolymers.



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ABSTRACT

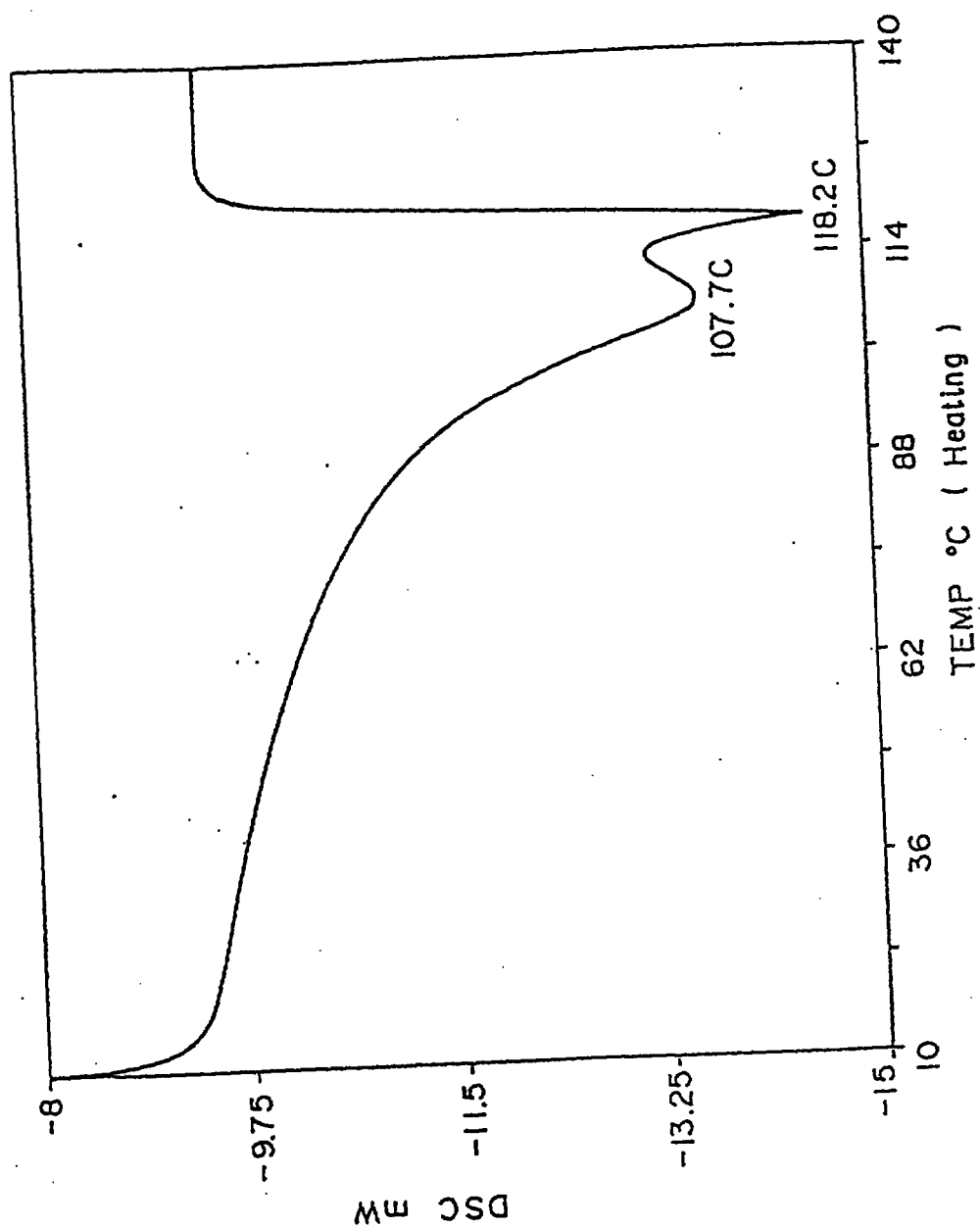
CATALYST FOR COPOLYMERIZING ETHYLENE WITH α -OLEFIN AND PROCESS FOR PRODUCING ETHYLENE- α -OLEFIN COPOLYMER USING THE CATALYST

A catalyst for copolymerizing ethylene with an α -olefin comprising a reaction product (A) of a titanium compound (A1) having at least one titanium-nitrogen bond with an organomagnesium compound (A2) and an organo-aluminum compound (B), said reaction product (A) being in the form of a liquid. The present invention can provide a catalyst having a high activity per unit weight of transition metal and an ethylene- α -olefin copolymer having narrow composition distribution and a high molecular weight and excellent in weather resistance, color development, transparency, corrosiveness and mechanical properties.

(FIG. 6)

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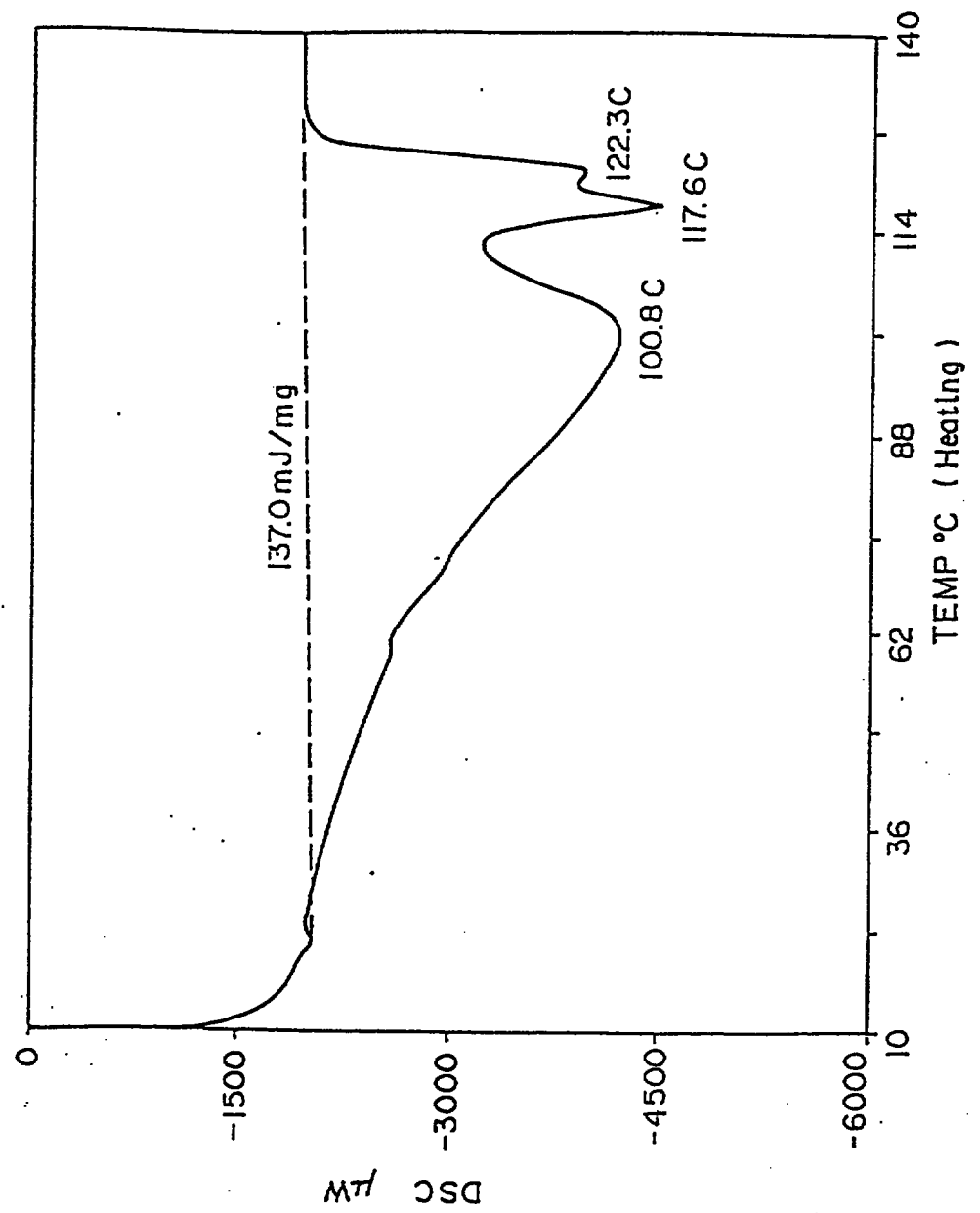
FIG. 1



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FIG. 2



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FIG. 3

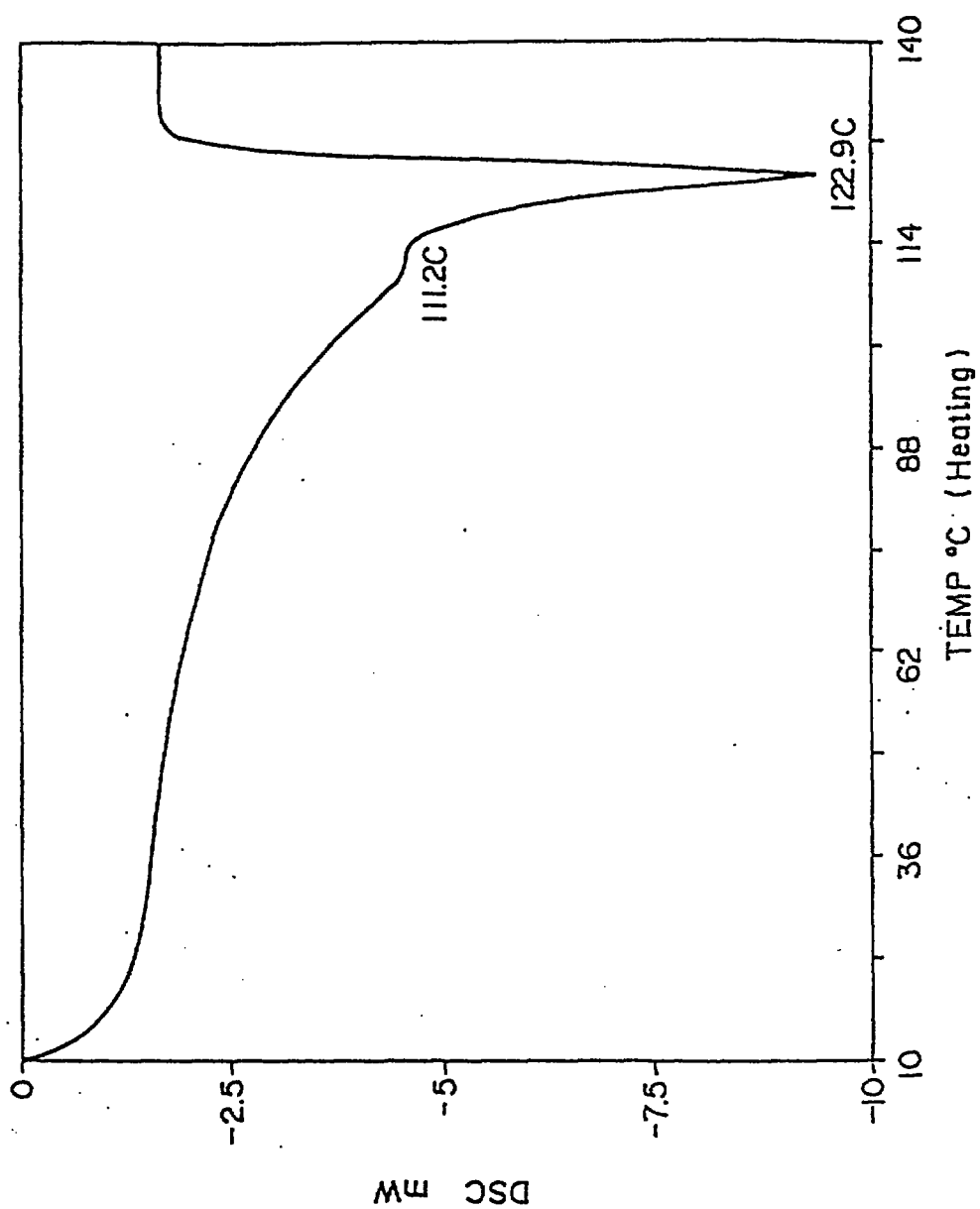
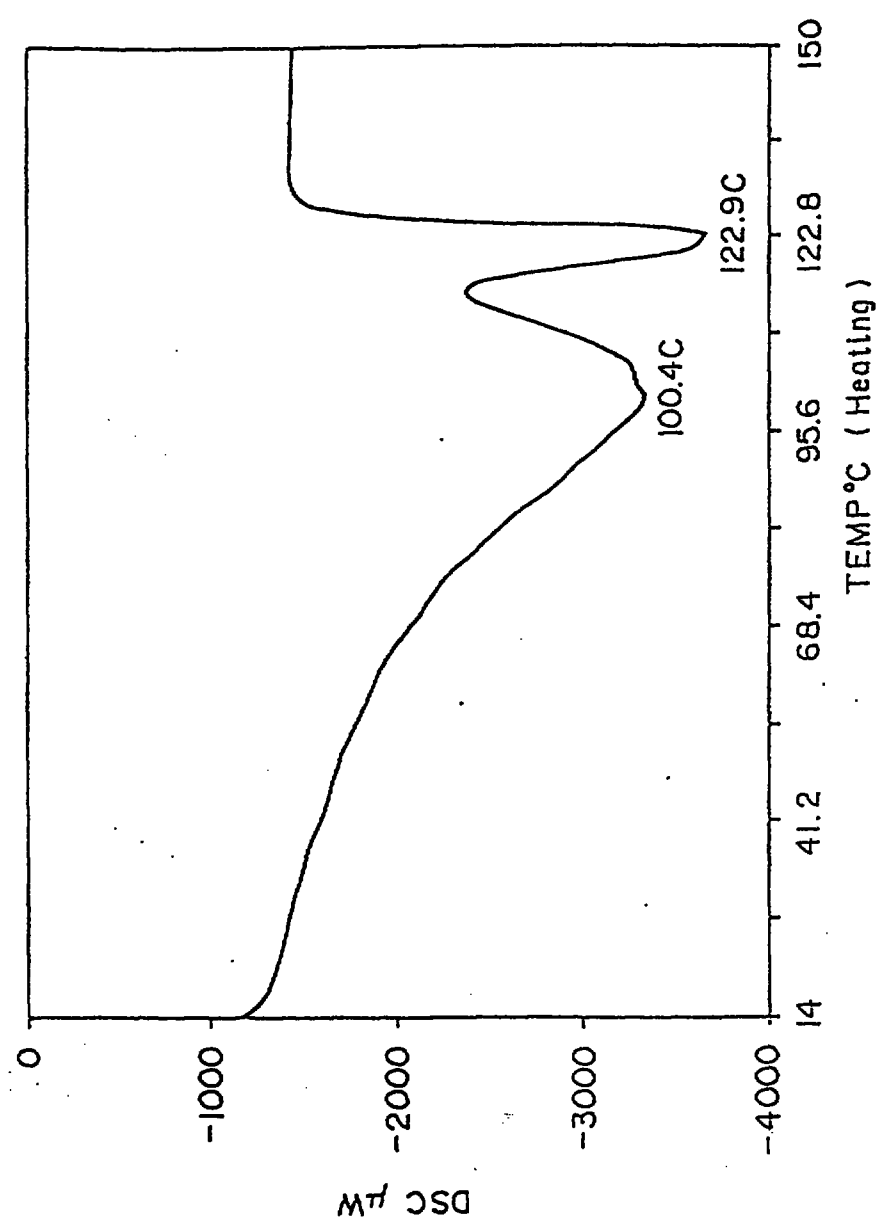


FIG. 4



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FIG. 5

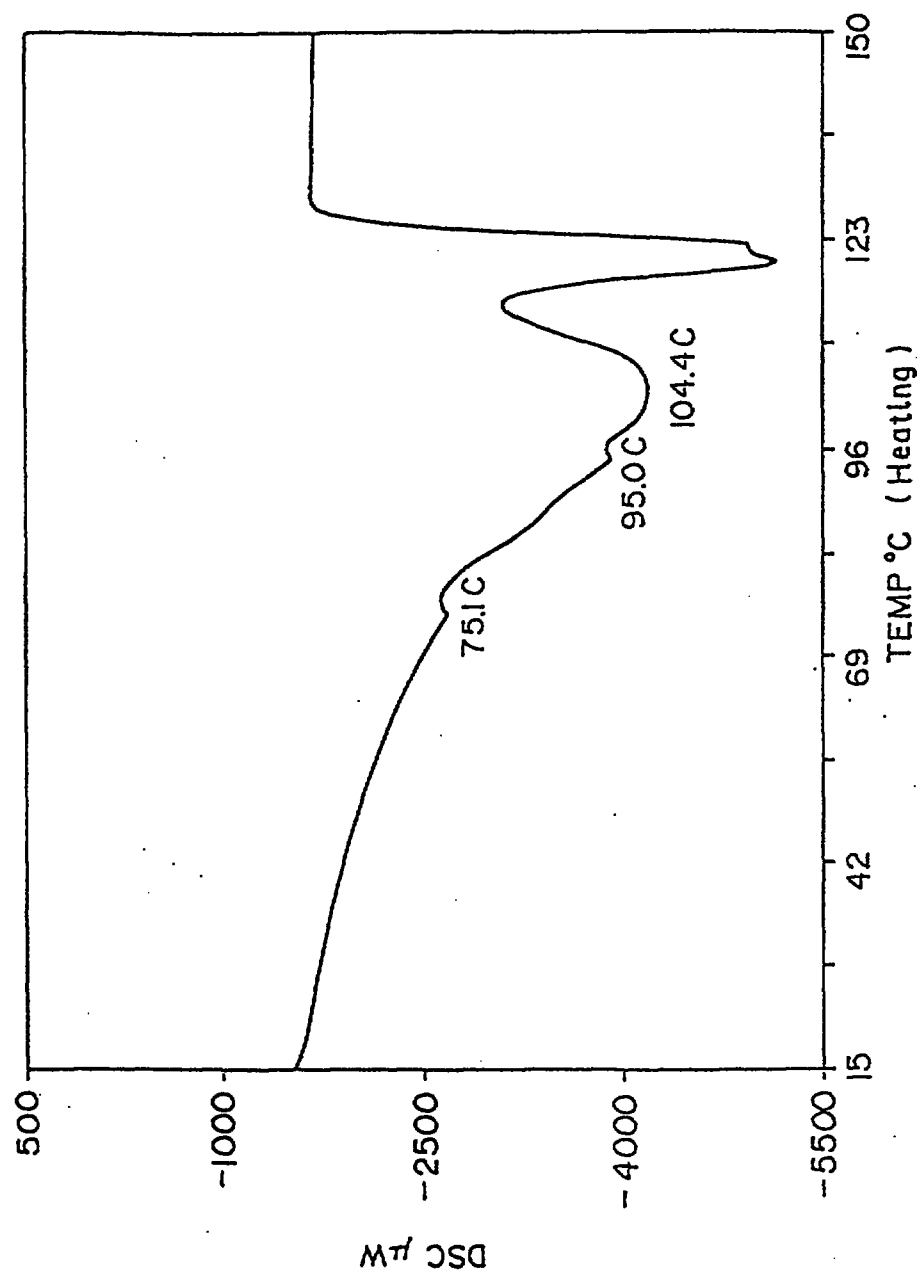
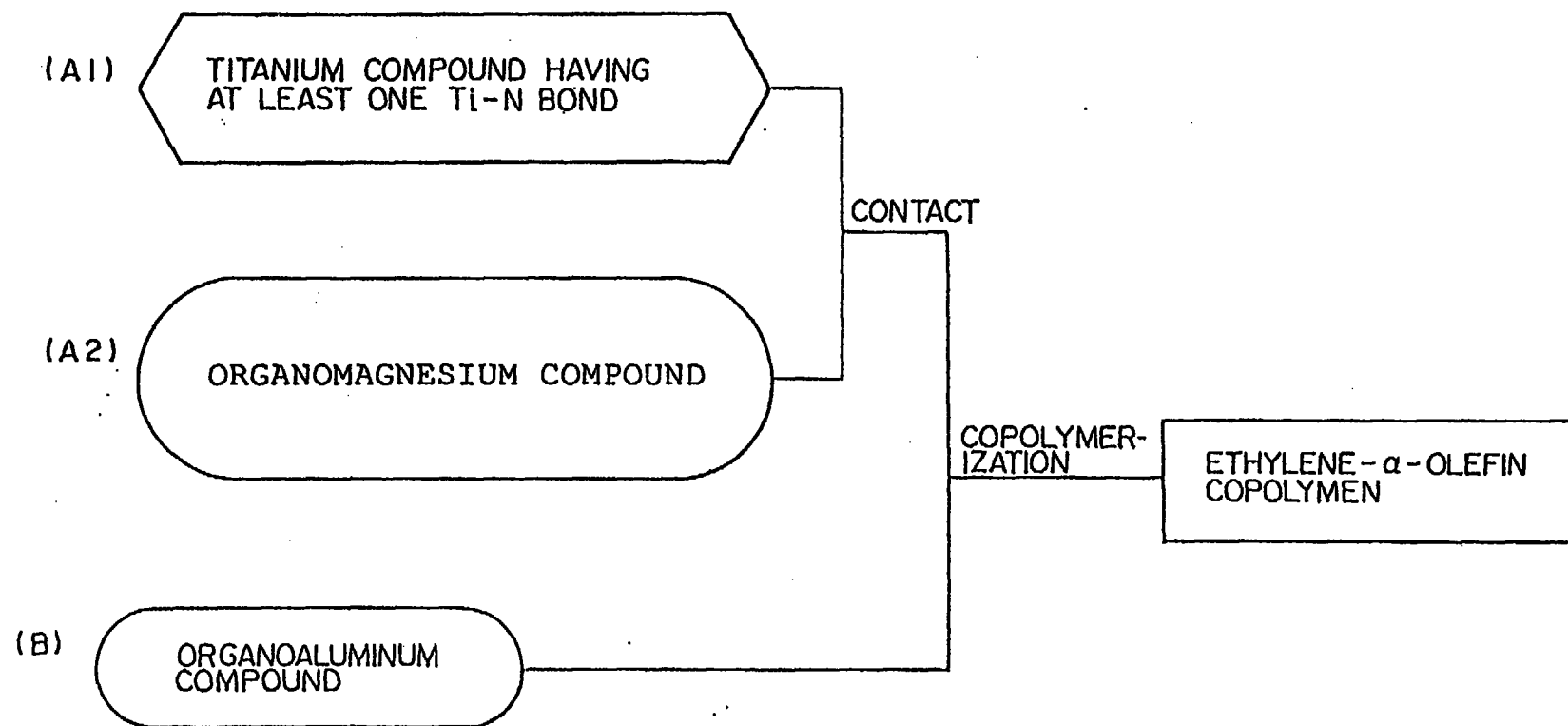


FIG. 6

(A) REACTION PRODUCT



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