

## Description

The present invention relates to a solid catalyst component for use in the polymerization of  $\alpha$ -olefins, a catalyst system containing said solid catalyst component, a process for producing  $\alpha$ -olefin polymers using said catalyst system and polymers obtained by said process. More particularly, the invention relates to a process for producing  $\alpha$ -olefin polymers, particularly granular elastomers and granular thermoplastic elastomers, having a high bulk density and a low content of fine powder by the process of slurry polymerization, bulk polymerization and gas phase polymerization by the use of a solid catalyst component having a high activity per one transition metal atom, wherein the procedure for removing the catalyst residue and amorphous polymer is unnecessary and the particle form of the solid catalyst component is controlled quite satisfactorily.

As is well known generally, the so-called Ziegler-Natta catalyst, composed of a compound of a transition metal belonging to Group IV to VI of the periodic table and an organometallic compound of a metal belonging to Group I to III of the periodic table is used in the process for producing polymers of  $\alpha$ -olefins such as propylene or butene-1.

Particularly in the industrial production of  $\alpha$ -olefin polymers, titanium trichloride catalyst is extensively used.

However, in the above-mentioned process, an amorphous polymer is formed as a by-product in addition to the industrially valuable, highly stereospecific  $\alpha$ -olefin polymer.

This amorphous polymer has poor industrial use and exercises a highly adverse influence upon the mechanical properties of the  $\alpha$ -olefin polymer when the latter is used in processed articles such as film and fiber.

Further, the formation of the amorphous polymer is also disadvantageous from the industrial point of view, in that it incurs a loss in the starting monomer and necessitates the presence of a particular apparatus for removing the amorphous polymer.

Accordingly, if the formation of the amorphous polymer can be eliminated or suppressed to a very slight quantity, it will bring about a great advantage.

On the other hand, the  $\alpha$ -olefin polymers obtained by such polymerization processes contain a residual portion of catalyst, which incurs various problems as far as stability, processability, and so on are concerned. Thus it is necessary to provide a particular apparatus for removal of the catalyst residue and stabilization.

This disadvantage can be overcome if the catalyst has a high activity expressed by the weight of formed  $\alpha$ -olefin polymer per unit weight of catalyst. If such a catalyst is used, the apparatus for removing the catalyst residue becomes unnecessary, which reduces the production cost of  $\alpha$ -olefin polymer.

Previously [Japanese Patent Application Kokai (Laid-Open) No. 61-287,904 (U.S. Patent 4,872,050)], the present inventors found that a catalyst system composed of:

(1) a trivalent titanium compound-containing a solid catalyst component obtainable by treating a solid product, which is obtained by reducing a titanium compound represented by general formula  $Ti(OR')_nX_{4-n}$  ( $R'$  represents a hydrocarbon residue having 1 to 20 carbon atoms,  $X$  represents a halogen atom, and  $n$  represents a number satisfying  $0 < n \leq 4$ ) with an organomagnesium compound in the presence of an organic silicon compound having a Si-O bond, with an ester compound and a mixture of an ether compound and titanium tetrachloride;

(2) an organoaluminum compound; and

(3) a silicon compound having a Si-OR" bond ( $R''$  represents a hydrocarbon residue having 1 to 20 carbon atoms) exhibits a high activity and a high specificity in the polymerization of  $\alpha$ -olefins.

However, when a solid catalyst such as Ziegler-Natta catalyst is put to industrial practical use, the form of the catalyst particle plays a very important role in controlling the bulk density of the polymer, the dimension of the polymer particle and its fluidity. The particle form of the solid catalyst of the above-mentioned invention was not yet satisfactory.

In the polymerization of ethylene, some attempts to improve the particle form by using a solid catalyst prepared by supporting a titanium-magnesium compound on silica gel have been published. [Japanese Patent Application Kokai (Laid-Open) Nos. 54-148,093 and 56-47,407 (U.S. Patent 4,315,999)].

Further, the present inventors have also proposed a method for improving the properties of particles by using a solid catalyst prepared by impregnating silica gel with a titanium-magnesium compound [Japanese Patent Application Kokai (Laid-Open) No. 62-256802]. Although the form of the particles can be greatly improved by these methods, the silica gel used as a carrier remains largely in the product, which causes fish-eyes in films and deteriorates the quality of the product.

On the other hand, olefinic thermoplastic elastomers have hitherto been produced by firstly producing a polypropylene or other olefin resins and an olefinic copolymer rubber such as ethylene-propylene rubber or the like separately, and then blending them together. As is well known, however, such a process is disadvantageous from the viewpoint of cost because olefin copolymer rubbers are generally produced by a solution polymerization process and the process for blending the olefinic copolymer rubber with an olefin resin requires a large amount of power and therefore a large quantity of energy.

On the other hand, a direct production of thermoplastic elastomer by a two-step slurry polymerization process under specified conditions was proposed in Japanese Patent Application Kokai (Laid-Open) Nos. 55-80,418 and 57-61,012 (U.S. Patent 4,489,195). However, this process was also disadvantageous in that the ethylene-propylene random copolymer largely dissolved into the solvent to enhance the system viscosity, which made the removal of polymerization heat quite difficult, and promoted adhesion between polymer particles, and thus made it difficult to carry out the production process stably. As a method for solving this problem, random copolymerization of ethylene and propylene at an extremely low temperature (below 30°C) was proposed. However, this method was also disadvantageous as catalyst activity was low under such a condition and a large-sized refrigerating equipment had to be used to remove the heat of polymerization, so that it was uneconomical.

Further, in Japanese Patent Application Kokai (Laid-Open) No. 59-105,008 (Canadian Patent 1,219,996), a production process of thermoplastic elastomers by a gas phase two-step polymerization was proposed. Although in this process an inorganic oxide such as silica gel was used as the carrier for the solid catalyst component in order to decrease the adhesive force of polymer particles, the improving effect was yet unsatisfactory.

Olefinic elastomers are generally produced by the solution polymerization process. The solution polymerization process requires many steps such as a step for recovering the unreacted monomer, a step for removing ashes, a step for stripping, etc. and the resulting polymer exists in the state of a solution, so that the system is highly viscous, difficult to stir and not easily controlled thermally, and therefore this process is quite disadvantageous from the viewpoint of production cost.

As a method for solving such problems, slurry polymerization of ethylene and propylene, i.e. their random copolymerization in liquefied propylene, was proposed in Japanese Patent Application Kokai (Laid-Open) No. 59-71,306. Although this process has improved productivity, it has to be carried out at an extremely low temperature (below 40°C) and therefore involves various problems such as a decrease in catalyst activity, and necessitates the use of a large-sized refrigerating equipment to remove polymerization heat, etc. which all is disadvantageous industrially.

Further, direct production of olefinic elastomers by gas phase polymerization was proposed in Japanese Patent Application Kokai (Laid-Open) No. 59-230,011 (Canadian Patent 1,219,400). However, in this process, a low polymerization temperature must be adopted and the monomer to be polymerized must be diluted with a very large amount of inert gas such as nitrogen or the like to prevent adhesion of polymer particles and to stably carry out the gas phase polymerization. Thus, this process has low productivity and is disadvantageous industrially.

EP-A-120734 discloses in Example 2 (b) that an amorphous ethylene-propylene random copolymer can be produced by means of gas phase polymerization at a temperature of 75°C by using an active solid hydrocarbon prepared by prepolymerization with an olefin in the gas phase. The resulting copolymer is in the form of a powder (particle size about 1000 µm). The active solid hydrocarbon is obtained by combining three components, i.e. a granular Ti component of 0.1 to 500 µm, a powder like porous organic solid carrier and an organometal compound in liquid phase; see Example 2 (a).

The art of said reference is similar to the present invention in that an amorphous polymer is obtained by means of gas phase polymerization at a high temperature. However, in order to obtain said result, said reference requires the following procedures:

(1) An active linear low density polyethylene is prepared in advance by subjecting a homogeneous fine powder composition (conventional solid catalyst component) to prepolymerization with an olefin, which is then used for the main polymerization.

(2) An inert gas such as N<sub>2</sub> coexists in a gas phase polymerization system in order to lower the adhesive properties of the resulting polymer particles.

These procedures are, of course, not preferable because they reduce the economical efficiency of the polymerization process.

US-A-4,618,595 discloses a polymerization process resulting in a relatively low amount of fines in the resulting polyethylene resin by carrying out the polymerization of ethylene using a solid catalyst component which is obtained by supporting a Ziegler catalyst component on polymer fibrils. The effect for decreasing the amount of polymer fines is one of the features of the present invention. However, the first characteristic

feature of the present invention resides in that a granular polyolefin elastomer having a low density can be obtained by means of a gas phase polymerization at a high temperature without causing adhesion among the polymer particles. Such a feature can be realized for the first time according to the present invention by using a porous polymer carrier having a specified structure.

5 US-A-4,477,639 describes in the Example the production of polypropylene using a solid catalyst component obtained by treating, with  $\text{TiCl}_4$ , a magnesium-modified polymer which is isolated from a homogeneous solution of magnesium benzoate and a vinyl chloride-vinylidene chloride copolymer. The technique described by this reference has no relation to "the physical characteristics of the polymer particles", and it is characterized by obtaining a solid catalyst component by utilizing a chemical action  
10 between the chlorine atoms contained in the polymer carrier and the Mg compound as mentioned in the specification.

Under the above-mentioned circumstances, the problem to be solved by the present invention, i.e., an object of the present invention, is to provide a polymerization catalyst having so high catalytic activity as to make the removal of catalyst residue and amorphous polymer unnecessary, a process for producing  $\alpha$ -olefin polymers using said catalyst, which are  $\alpha$ -olefin polymers having a high bulk density and a low  
15 content of fine powder and containing no inorganic oxides such as silica gel causing fish-eyes when the polymer is used as a film.

Further, another object of the present invention is to solve the above-mentioned problems which appeared in the prior art and to thereby provide a process for producing a granular olefinic thermoplastic elastomer and a granular olefinic elastomer of improved performances by a gas phase polymerization process. Another object of the present invention is to provide olefinic granular thermoplastic elastomers and granular elastomers obtainable by said polymerization process.

Ethylene-propylene rubbers and the like contain a large quantity of polymers having low crystallinity and their polymer particles are highly adhesive in general. Thus in the case of these polymers, it is difficult  
25 to carry out gas phase polymerization stably.

As the gas phase polymerization reactor for  $\alpha$ -olefins, a stirring-mixing tank type reactor, a fluidized bed type reactor, and a fluidized bed type reactor having a stirrer, have hitherto been proposed. As the adhesive force of polymer particles increases in the stirring type reactors, extreme high power is required for achieving the desired stirring speed, and design of such apparatuses is remarkably difficult. Further, in  
30 such a state, uniform mixing is difficult to achieve and high temperature regions remain in some localities, due to which a part of the polymer forms a bulky mass and thereby injures the stirrer and the thermometer in the reactor and makes it difficult to withdraw the polymer particles from the reactor via the piping.

On the other hand, in reactors in which unreacted monomer is polymerized in a fluid state, there is a tendency for slugging which increases remarkably the quantity of polymer particles flying onto the gas circulation line and causes deposition on lines and their clogging.  
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Further, in such a state, stirring may result in a partial formation of polymer mass which represents a problem.

Further, when the polymer particles have a high adhesive force, clogging readily takes place in the piping for transporting the particles. Further, bridging takes place in the under part of the cyclone or in the hopper, which makes it difficult to withdraw the particles stably.

Thus, it has been quite difficult to produce a polymer containing a large quantity of polymer having low crystallinity by gas phase polymerization process, in spite of the advantage of gas phase polymerization of not having to use a solvent for dissolving the polymer having low crystallinity.

Further, in an improved gas phase polymerization process, the removal of catalyst residue is substantially omitted. Thus, the catalyst system used therein must be highly improved in polymerization activity.  
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The present inventors have solved the above-mentioned problems by the use of a specified catalyst system, and found an effective process for producing an olefinic granular thermoplastic elastomer and a granular elastomer having excellent performances by gas phase polymerization.

Thus, the present invention provides:

50 a solid catalyst component (A) for  $\alpha$ -olefin polymerization containing as catalyst components at least titanium, magnesium and chlorine which are impregnated into an organic porous polymer carrier having a mean particle diameter of 5 to 1,000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to 5,000  $\cdot 10^{-10}\text{m}$  (100 to 5,000  $\text{\AA}$ );

a catalyst system comprising at least said solid catalyst component (A) and an organoaluminum  
55 compound (B); and

a process for producing a granular thermoplastic elastomer and a granular elastomer which comprises polymerizing an  $\alpha$ -olefin or copolymerizing  $\alpha$ -olefins by the use of said catalyst system according to either of the following processes 1) to 3) to obtain an olefinic polymer:

1) a process which comprises, in the first step, preparing an isotactic polypropylene by a polymerization reaction in liquefied propylene and/or in gas phase, followed by, in the second step, preparing an ethylene- $\alpha$ -olefin random copolymer in the gas phase so that the ethylene content in the copolymer formed in the second step comes to 5 to 95% by weight and its intrinsic viscosity in tetralin at 135°C comes to 0.3 to 10 and the weight of the copolymer formed in the second step comes to 60 to 97% by weight based on the total weight of the polymers;

2) a process which comprises, in the first step, slurry polymerizing ethylene in a propane solvent or a butane solvent or polymerizing ethylene in the gas phase, followed by, in the second step, preparing an ethylene- $\alpha$ -olefin random copolymer by a polymerization reaction in the gas phase so that the ethylene content in the copolymer formed in the second step comes to 5 to 95% by weight and its intrinsic viscosity in tetralin at 135°C comes to 0.3 to 10 and the weight of the copolymer formed in the second step comes to 60 to 97% by weight based on the total weight of the polymers;

3) a process which comprises carrying out a random copolymerization of ethylene and  $\alpha$ -olefin in the gas phase so that the ethylene content in the copolymer thus formed comes to 5 to 95% by weight and its intrinsic viscosity in tetralin at 135°C comes to 0.3 to 10; and an olefinic granular thermoplastic elastomer or a granular elastomer obtained by said process.

Figure 1 is a particle size distribution curve of polypropylene powder, wherein (A), (B) and (C) each expresses the particle size distribution curve of the polypropylene powder obtained in Example 21, Example 22 and Comparative Example 12, respectively.

Figure 2 is a flow chart for better understanding of the present invention. This flow chart is a typical example of the embodiments of the present invention, and the invention is by no means limited by this flow chart.

Next, details of the present invention will be described below.

#### (I) Solid Catalyst Component (A)

The solid catalyst component used in the present invention is prepared by impregnating an organic porous polymer carrier having a mean particle diameter of 5 to 1,000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to 5,000  $\cdot 10^{-10}\text{m}$  (100 to 5,000 Å) with a catalyst component comprising at least titanium, magnesium and chlorine.

The performance required of the catalyst of the invention include that it can exhibit a sufficiently high activity and form a copolymer having good properties in a random copolymerization of ethylene and  $\alpha$ -olefin, that it can form polymer particles having good particle characteristics. Further, when a multistage polymerization is carried out and, in this process, a polymer constituted mainly of polypropylene is to be formed, the catalyst is required to exhibit a more enhanced stereospecificity.

According to a study of the present inventors, when a solid catalyst component having so high a catalyst activity that the formation of total polymer per 1 g titanium atom in the solid catalyst component is  $5 \times 10^4$  g or above, preferably  $7.5 \times 10^4$  g or above and particularly preferably  $10 \times 10^4$  g or above is used, a thermoplastic elastomer can be obtained without any substantial step for removing the catalyst residue, and this is advantageous.

When a homopolymerization of propylene is carried out, it is preferable to use a catalyst system such that the polypropylene obtained therefrom has a stereospecificity of 10% by weight or below, preferably 7% by weight or below and particularly 5% by weight or below, as expressed by the content of xylene-soluble fraction (at 20°C), i.e. the weight of atactic polypropylene, in the resulting polypropylene, from the viewpoint of properties of copolymer.

The mean particle diameter of the solid catalyst component is an important factor when producing a copolymer having good particle characteristics. That is, the mean particle diameter of the solid catalyst component should be 5 to 1,000  $\mu\text{m}$ , preferably 10 to 600  $\mu\text{m}$ , and particularly 15 to 500  $\mu\text{m}$ .

If the mean particle diameter is smaller than 5  $\mu\text{m}$ , the adhesive force of polymer particles increases and, in a fluidized bed type gas phase reactor, the flying problem of catalyst and polymer particle arises. If the mean particle diameter is greater than 1,000  $\mu\text{m}$ , a stable state of flow cannot be realized in a fluidized bed type gas phase reactor because the minimum velocity of fluidization markedly increases and, as its result, the polymer particles tend to form a mass.

Next, the solid catalyst component will be illustrated in more detail.

## (a) Titanium Compound

The titanium compound used for the synthesis of the solid catalyst component used in the invention is represented by general formula  $Ti(OR^1)_aX_b$ , wherein  $R^1$  represents a hydrocarbon residue having 1 to 20 carbon atoms, X represents a halogen atom, and a and b represent numbers satisfying  $0 \leq a \leq 4$ ,  $0 \leq b \leq 4$  and  $a + b = 3$  or 4.

Next, a particular case in which a titanium compound represented by general formula  $Ti(OR^1)_nX_{4-n}$ , wherein n represents a hydrocarbon residue having 1 to 20 carbon atoms, X represents a halogen atom and n represents a number satisfying  $0 < n \leq 4$ , is used will be mentioned. Concrete examples of  $R^1$  include alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, isoamyl, n-hexyl, n-heptyl, n-octyl, n-decyl or n-dodecyl; aryl groups such as phenyl, cresyl, xylyl or naphthyl; cycloalkyl groups such as cyclohexyl or cyclopentyl; allyl groups such as propenyl group; and aralkyl groups such as benzyl.

Among them, alkyl groups having 2 to 18 carbon atoms and aryl groups having 6 to 18 carbon atoms are preferable, and straight chain alkyl groups having 2 to 18 carbon atoms are particularly preferable.

It is also possible to use a titanium compound having two or more different  $OR^1$  groups.

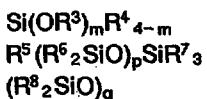
Examples of said halogen atom represented by X include chlorine, bromine and iodine, among which chlorine gives a particularly good result.

As the method for synthesizing the titanium compound represented by general formula  $Ti(OR^1)_nX_{4-n}$  ( $0 < n \leq 4$ ), any of the well known methods may be adopted. For example, a method which comprises reacting  $Ti(OR^1)_4$  and  $TiX_4$  at a specified ratio and a method which comprises reacting  $TiX_4$  and the corresponding alcohol at a specified ratio can be adopted.

Concrete examples of the compound represented by the aforementioned general formula  $Ti(OR^1)_aX_b$ , which can preferably be used in the present invention include titanium trichloride, ethoxytitanium dichloride, butoxytitanium dichloride, titanium tetrachloride, ethoxytitanium trichloride, butoxytitanium trichloride, phenoxytitanium trichloride, dibutoxytitanium dichloride, diphenoxytitanium dichloride, tributoxytitanium chloride, tetraethoxytitanium, tetrabutoxytitanium and tetraphenoxytitanium.

## (b) Organosilicon Compound Having a Si-O Bond

The organosilicon compound having a Si-O bond which is optionally used in the synthesis of component (A) of the present invention, may be represented by the following general formulas



wherein  $R^3$  represents a hydrocarbon residue having 1 to 20 carbon atoms;  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  each represents a hydrocarbon residue having 1 to 20 carbon atoms or a hydrogen atom; m represents a number satisfying  $0 < m \leq 4$ ; p is an integer of 1 to 1,000; and q is an integer of 2 to 1,000.

Concrete examples of said organosilicon compound include the followings:

tetramethoxysilane, dimethyldimethoxysilane, tetraethoxysilane, triethoxyethylsilane, diethoxydiethylsilane, ethoxytriethylsilane, tetraisopropoxysilane, diisopropoxydiisopropylsilane, tetrapropoxysilane, dipropoxydipropylsilane, tetra-n-butoxysilane, di-n-butoxy-di-n-butylsilane, dicyclopentoxymethylsilane, diethoxydiphenylsilane, triethoxyphenylsilane, hexamethyldisiloxane, hexaethyldisiloxane, hexapropyldisiloxane, octaethyltrisiloxane, dimethylpolysiloxane, diphenylpolysiloxane, methylhydropolysiloxane and phenylhydropolysiloxane.

Among these organosilicon compounds, alkoxysilane compounds represented by general formula  $Si(OR^3)_mR^{4-4-m}$  are preferable wherein m is preferably a number satisfying  $1 \leq m \leq 4$ . Among them, tetraalkoxysilane compounds ( $m = 4$ ) are particularly preferable.

## (c) Magnesium Compound

Next, as the magnesium compound, the followings are used.

As the reductive compound having magnesium-carbon bond, Grignard compounds represented by the general formula  $R'MgX$  (wherein  $R'$  is a hydrocarbon group of 1 to 20 carbon atoms and X is a halogen atom) and dialkyl- or diaryl-magnesium compounds represented by the general formula  $R''R'''Mg$  (wherein  $R''$  and  $R'''$  are each a hydrocarbon group of 1 to 20 carbon atoms) are used preferably.  $R'$ ,  $R''$  and  $R'''$  may be same or different and are each of the alkyl, aryl, aralkyl or alkenyl group such as methyl, ethyl, n-

propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-amyl, isoamyl, n-hexyl, n-octyl, 2-ethylhexyl, phenyl or benzyl.

As the reductive compound having magnesium-hydrogen bond, alkylmagnesium hydride is used preferably.

Concrete examples of the above-mentioned compounds include the followings: diethylmagnesium, dibutylmagnesium, dihexylmagnesium, ethylmagnesium chloride, butylmagnesium chloride, hexylmagnesium chloride, butylethoxymagnesium and butylmagnesium hydride and are preferably used. These magnesium compounds may be used in the form of a complex compound with an organoaluminum compound. On the other hand, preferable examples of non-reductive magnesium compound include magnesium dihalogenides such as magnesium dichloride or magnesium dibromide; alkoxymagnesium compounds such as methoxymagnesium chloride, ethoxymagnesium chloride, butoxymagnesium chloride, phenoxymagnesium chloride, diethoxymagnesium, dibutoxymagnesium or diphenoxymagnesium; and magnesium carboxylates such as magnesium laurate or magnesium stearate.

Said non-reductive magnesium compound may also be a compound which has been derived from a reductive magnesium compound by known process either previously or at the time of preparing the solid catalyst.

#### (d) Organic Porous Polymer Carrier

Examples of the organic porous polymer carrier used in the solid catalyst component (A) of the present invention include the polystyrene type, polyacrylic ester type, polymethacrylic ester type, polyacrylonitrile type, polyvinylchloride type and polyolefin type of porous polymer beads. Concrete examples of the material constituting the carrier include polystyrene, styrene-divinylbenzene copolymer, styrene-N,N'-alkylenedimethacrylamide copolymer, styrene-ethyleneglycol methyldimethacrylate copolymer, polymethylacrylate, polyethylacrylate, methylacrylate-divinylbenzene copolymer, ethylacrylate-divinylbenzene copolymer, polymethylmethacrylate, methylmethacrylate-divinylbenzene copolymer, polyethyleneglycol methyldimethacrylate, polyacrylonitrile, acrylonitrile-divinylbenzene copolymer, polyvinylchloride, polyvinylpyrrolidine, polyvinylpyridine, ethylvinylbenzene-divinylbenzene copolymer, polyethylene, ethylene-methylacrylate copolymer and polypropylene.

Among the porous polymer beads of these materials, those of polystyrene, polyvinylchloride, polyolefin and polyacrylonitrile are preferable, and those of polystyrene, styrene-divinylbenzene copolymer and polyvinylchloride are more preferable.

The mean particle diameter of the porous polymer beads is 5 to 1,000  $\mu\text{m}$ , preferably 10 to 600  $\mu\text{m}$ , and particularly 15 to 500  $\mu\text{m}$ . Further, as measured in the pore radius range of 100 to  $5,000 \cdot 10^{-10}\text{m}$  (100 to 5,000 Å), its pore volume is 0.1 ml/g or above, preferably 0.2 ml/g or above, and particularly 0.25 ml/g or above.

The porous polymer is preferably put to use after removing the adsorbed water. Concretely saying, a porous polymer is dried under reduced pressure at a temperature of about 80 °C or above and then put to use. Otherwise, it is dried at a temperature of about 60 °C or above and then treated with an organometallic compound such as organomagnesium and then put to use.

#### (e) Ester Compound

As the ester compound optionally used in the synthesis of component (A) of the present invention, monobasic and polybasic carboxylic esters, including aliphatic carboxylic esters, olefinic carboxylic esters, alicyclic carboxylic esters and aromatic carboxylic esters, are used. Concrete examples of said ester compound include methyl acetate, ethyl acetate, phenyl acetate, methyl propionate, ethyl propionate, ethyl butyrate, ethyl valerate, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl benzoate, butyl benzoate, methyl toluate, ethyl toluate, ethyl anisate, diethyl succinate, dibutyl succinate, diethyl malonate, dibutyl malonate, dimethyl maleate, dibutyl maleate, diethyl itaconate, dibutyl itaconate, monoethyl phthalate, dimethyl phthalate, methyl ethyl phthalate, diethyl phthalate, di-n-propyl phthalate, diisopropyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-n-heptyl phthalate, di-n-octyl phthalate and diphenyl phthalate.

Among these ester compounds, olefinic carboxylic esters such as methacrylic ester or maleic esters and phthalic esters are preferable, and phthalic diesters are particularly preferable.

## (f) Ether Compound

The ether compound is used optionally in the synthesis of component (A) of the present invention. Preferable examples of the ether compound include dialkyl ethers such as diethyl ether, di-n-propyl ether, diisopropyl ether, di-n-butyl ether, di-n-amyl ether, diisoamyl ether, dineopentyl ether, di-n-hexyl ether, di-n-octyl ether, methyl n-butyl ether, methyl isoamyl ether and ethyl isobutyl ether.

Among them, di-n-butyl ether and diisoamyl ether are particularly preferable.

## (g) Synthesis of Solid Catalyst Component (A)

The catalyst component comprising at least titanium, magnesium and chlorine used for impregnation of the organic porous polymer carrier will be explained concretely.

In the catalyst component of the present invention, the titanium/magnesium atomic ratio is 0.01 to 0.8 and preferably 0.02 to 0.2. The chlorine/magnesium atomic ratio is 1.8 to 10 and preferably 2.0 to 5.0.

Methods for preparing such a catalyst component, are disclosed in, for example, Japanese Patent Publication No. 35-495, Japanese Patent Application Kokai (Laid-Open) No. 46-4393, Japanese Patent Publication No. 46-31330, Japanese Patent Application Kokai (Laid-Open) No. 47-42283, Japanese Patent Application Kokai (Laid-Open) No. 49-86483, Japanese Patent Publication No. 57-24361, Japanese Patent Application Kokai (Laid-Open) No. 61-296,007, and Japanese Patent Publication Nos. 39-12105, 43-13050, 46-34092, 46-34098, 47-41676 and 55-23561.

Next, as the method for impregnating the organic porous polymer carrier with the catalyst component, mechanical methods such as pulverization and chemical methods in slurry state can be adopted. Among these methods, chemical methods are more preferable from the viewpoint of characteristic properties of particles.

As a concrete example of the above-mentioned method, the method comprising impregnating a porous carrier such as silica gel with the catalyst component, disclosed in Japanese Patent Application Kokai (Laid-Open) Nos. 52-42585, 54-148093, 56-47407, 59-230006 and 61-37803, for example, can be adopted.

As examples of said method, the following methods can be referred to:

(1) A method which comprises treating a porous carrier with an organomagnesium compound such as Grignard reagent and then treating it with  $TiCl_4$  or the like.

(2) A method which comprises treating a porous carrier with an organomagnesium compound such as a Grignard reagent, followed by reacting it with a halogenating agent and/or an alcohol and then treating it with a titanium compound such as  $TiCl_4$ .

(3) A method which comprises dissolving a magnesium halide compound and/or an alkoxymagnesium compound into a donor such as an alcohol, an ether or the like, followed by forming it into a complex compound with  $TiCl_4$  and then impregnating it into a porous carrier.

(4) A method which comprises dissolving a magnesium halide compound and/or an alkoxymagnesium compound into a donor such as an alcohol or an ether, followed by impregnating it into a porous carrier and then treating it with a titanium compound such as  $TiCl_4$ .

(5) A method which comprises reducing an alkoxytitanium compound with an organomagnesium compound such as a Grignard reagent in the presence of a porous carrier and then treating it with a mixture of an ether compound and titanium tetrachloride.

Among these methods, the method (5) is preferable, and a method which comprises reducing an alkoxytitanium compound with an organomagnesium compound such as a Grignard reagent in the presence of an organosilicon compound having a Si-O bond and an organic porous polymer carrier to obtain a solid product and then treating it with a mixture of an ether compound and titanium tetrachloride or treating it with an ester compound and a mixture of an ester compound and titanium tetrachloride is more preferable.

The amount of the catalyst component to be impregnated into the organic porous polymer carrier is 1 to 70% by weight, preferably 3 to 60% by weight and particularly 5 to 55% by weight, as expressed by the content in the resulting solid catalyst component. If the amount of catalyst component impregnated into organic porous polymer carrier is too much, particle characteristics of the polymer are deteriorated. If its amount is too small, the activity per unit weight of solid catalyst decreases.

Next, the above-mentioned methods will be mentioned in more detail.

As a concrete preparation example for producing the solid catalyst component of the present invention a method is explained below comprising reducing an alkoxytitanium compound with an organomagnesium compound in the co-presence of an organosilicon compound having a Si-O bond and an organic porous polymer carrier, treating the reduced titanium compound with an ester compound and then treating the ester-treated compound with an ether compound and titanium tetrachloride. The solid catalyst component of

the present invention is, however, not limited by the following explanation.

All the synthetic reactions are carried out in an atmosphere of inert gas such as nitrogen or argon.

Thus, the solid product is synthesized by reducing a titanium compound with an organomagnesium compound in the presence of an organosilicon compound having a Si-O bond and an organic porous polymer carrier. It is desired in this reaction that the solid formed by the reduction is deposited onto the particles of the porous polymer carrier and therefore the solid product retains the form of the porous polymer carrier without forming any fine powders.

As the method of reduction of the titanium compound with organomagnesium compound, a method which comprises adding an organomagnesium compound to a mixture consisting of a titanium compound, an organosilicon compound and porous polymer beads can be referred to, for example.

Preferably, the titanium compound, the organosilicon compound and the porous polymer beads are put to use after dissolving them into an appropriate solvent or diluting them with a solvent.

As said solvent, there can be referred to aliphatic hydrocarbons such as hexane, heptane, octane or decane; aromatic hydrocarbons such as toluene and xylene; alicyclic hydrocarbons such as cyclohexane, methylcyclohexane or decalin; and ether compounds such as diethyl ether, dibutyl ether, diisooamyl ether and tetrahydrofuran.

The temperature of the reduction is  $-50^{\circ}\text{C}$  to  $70^{\circ}\text{C}$ , preferably  $-30^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ , and particularly  $-25^{\circ}\text{C}$  to  $35^{\circ}\text{C}$ .

Though the dropping time is not critical, it is usually 10 minutes to 6 hours. If desired, a post-reaction may be carried out at a temperature of  $20^{\circ}\text{C}$  to  $120^{\circ}\text{C}$  after completion of the reduction.

The amount of the organosilicon compound is in the range of  $\text{Si/Ti} = 1$  to 50, preferably 3 to 30 and particularly 5 to 25, as expressed in terms of the atomic ratio of silicon atoms to titanium atoms (Si/Ti) in the titanium compound.

The amount of organomagnesium compound is in the range of  $(\text{Ti} + \text{Si})/\text{Mg} = 0.1$  to 10, preferably 0.2 to 5.0 and particularly 0.5 to 2.0, as expressed in terms of the atomic ratio of the sum of titanium atoms and silicon atoms to magnesium atoms  $(\text{Ti} + \text{Si})/\text{Mg}$ .

The amount of the porous polymer beads is such an amount that its weight in the solid product comes to 20 to 95% by weight and preferably 30 to 85% by weight.

The solid product formed by the reduction is separated from liquid phase and washed several times with an inert hydrocarbon solvent such as hexane or heptane.

Subsequently, the solid product obtained in the above-mentioned manner is treated with an ester compound.

The ester compound is used in an amount of 0.1 to 50 moles, preferably 0.3 to 20 moles, and particularly 0.5 to 10 moles, per one mole of the titanium atom in the solid product.

The ester compound is used in an amount of 0.01 to 1.0 mole and preferably 0.03 to 0.5 mole per one mole of magnesium atom in the solid product.

The treatment of the solid product with the ester compound can be carried out by any well known methods for contacting them together, such as slurry method or mechanical pulverization using a ball mill. Among these methods, however, mechanical pulverization is not preferable from the industrial point of view because it produces a large quantity of fine powder in the solid catalyst component and thereby broadens the particle size distribution. Preferably, both the materials are contacted in the presence of a diluent.

The diluents which can be used for this purpose include aliphatic hydrocarbons such as pentane, hexane, heptane and octane; aromatic hydrocarbons such as benzene, toluene or xylene; alicyclic hydrocarbons such as cyclohexane, cyclopentane and the like; and halogenated hydrocarbons such as 1,2-dichloroethane or monochlorobenzene. Among these diluents, halogenated hydrocarbons and aromatic hydrocarbons are particularly preferable.

The diluent is used in an amount of 0.1 ml to 1,000 ml and preferably 1 ml to 100 ml, per 1 g of the solid product. The temperature of the treatment is  $-50^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , and preferably  $0^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ . The duration of the treatment is 10 minutes or longer, and preferably 30 minutes to 3 hours. After completion of the treatment, the mixture is allowed to stand, the solid is separated from the liquid phase and it is washed several times with an inert hydrocarbon solvent. Thus, an ester-treated solid product is obtained.

The treatment with an ester compound may also be carried out simultaneously with the subsequent treatment with a mixture of an ether compound and titanium tetrachloride by using the ester compound in the presence of the mixture of the ether compound and titanium tetrachloride.

Next, the treatment of the ester-treated solid product with a mixture of an ether compound and titanium tetrachloride is preferably carried out in the state of a slurry. As the solvent for preparing the slurry, there can be referred to aliphatic hydrocarbons such as pentane, hexane, heptane, octane or decane; aromatic hydrocarbons such as toluene or xylene; alicyclic hydrocarbons such as cyclohexane, methylcyclohexane,

decalin and the like; and halogenated hydrocarbons such as dichlorethane, trichlorethane, trichlorethylene, monochlorobenzene, dichlorobenzene or trichlorobenzene.

The slurry concentration is 0.05 to 0.5 g-solid/ml-solvent and preferably 0.1 to 0.4 g-solid/ml-solvent.

The reaction temperature is 30°C to 150°C, preferably 45°C to 120°C, and particularly 60°C to 100°C.

Although the reaction time is not critical, a reaction time of 30 minutes to 6 hours is usually preferable.

The method for the addition of the ester-treated solid product, the ether compound and titanium tetrachloride may be any of the method which comprises adding the ether compound and titanium tetrachloride to the ester-treated solid product and the method which comprises adding the ester-treated solid product to a solution of the ether compound and titanium tetrachloride, in the reverse order.

In the method which comprises adding the ether compound and titanium tetrachloride to the ester-treated solid product, a method which comprises addition of the ether compound followed by addition of titanium tetrachloride or a method which comprises simultaneous addition of the ether compound and titanium tetrachloride is preferable, and a method which comprises adding a previously prepared mixture of an ether compound and titanium tetrachloride is particularly preferable.

The reaction between the ester-treated solid product and the ether compound and titanium tetrachloride may be repeated twice or more. From the viewpoint of catalyst activity and stereospecificity, it is preferable to repeat the reaction using the mixture of the ether compound and titanium tetrachloride at least twice.

The ether compound is used in an amount of 0.1 to 100 moles, preferably 0.5 to 50 moles, and particularly 1 to 20 moles per one mole of titanium atom in the solid product.

The amount of titanium tetrachloride to be added is 2 to 2,000 moles, preferably 10 to 1,000 moles, and particularly 30 to 800 moles per one mole of titanium atom in the solid product.

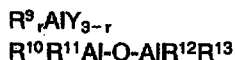
Per one mole of the ether compound, the amount of titanium tetrachloride to be added is 1 to 100 moles, preferably 1.5 to 75 moles and particularly 2 to 50 moles.

The trivalent titanium compound-containing solid catalyst component obtained in the above-mentioned manner is separated from liquid phase and washed several times with an inert hydrocarbon solvent such as hexane or heptane, after which it is put to use for polymerization.

From the viewpoint of catalyst activity and stereospecificity, it is preferable to separate the solid product from the liquid phase, wash it at least once with an excessive quantity of an aromatic hydrocarbon such as toluene or a halogenated hydrocarbon solvent such as monochlorobenzene at a temperature of 50°C to 120°C, then wash it repeatedly (several times) with an aliphatic hydrocarbon solvent such as hexane and then put it to use in the polymerization reaction.

## (II) Organoaluminum Compound (B)

The organoaluminum compound (B) used in the present invention in combination with the above-mentioned solid catalyst component (A) has at least one aluminum-carbon bond in one molecule. Its typical examples are those represented by the following general formulas:



wherein  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  each represents a hydrocarbon residue having 1 to 8 carbon atoms; Y represents a halogen atom, a hydrogen atom or an alkoxy group; and r represents a number satisfying  $2 \leq r \leq 3$ .

Concrete examples of the organoaluminum compound include trialkylaluminums such as triethylaluminum, triisobutylaluminum or trihexylaluminum; dialkylaluminum hydrides such as diethylaluminum hydride or diisobutylaluminum hydride; mixtures of trialkylaluminum and dialkylaluminum halide; and alkylalumoxanes such as tetraethyldialumoxane or tetrabutylalumoxane.

Among these organoaluminum compounds, trialkylaluminums, mixtures of trialkylaluminum and dialkylaluminum halide and alkylalumoxanes are preferable, and triethylaluminum, triisobutylaluminum, mixture of triethylaluminum and diethylaluminum chloride and tetraethyldialumoxane are particularly preferable.

Said organoaluminum compound is used in so widely ranging an amount as 1 to 1,000 moles per one mole of titanium atom in the solid catalyst. The particularly preferable range of its amount is 5 to 600 moles per one mole of titanium atom.

## (III) Electron Donor (C)

At the time of the polymerization reaction, a known electron donor may be added to the system for the purpose of regulating the molecular weight of the polymer or, in some cases, for improving the stereospecificity of the polymer. As said electron donor (C), a compound selected from organosilicon compounds having a Si-OR<sup>2</sup> bond (R<sup>2</sup> represents a hydrocarbon residue having 1 to 20 carbon atoms) or a Si-N-C bond, aromatic carboxylic ester compounds and sterically hindered amines are used.

As said organosilicon compound, alkoxysilane compounds represented by general formula R<sup>14</sup><sub>t</sub>Si(OR<sup>2</sup>)<sub>4-t</sub> (R<sup>14</sup> and R<sup>2</sup> each represents a hydrocarbon residue having 1 to 20 carbon atoms, and t represents a number satisfying 0 ≤ t ≤ 3) are preferably used.

Examples of the aromatic carboxylic ester include methyl benzoate, ethyl benzoate, n-propyl benzoate, isopropyl benzoate, n-butyl benzoate, phenyl benzoate, methyl toluate, ethyl toluate, methyl anisate, ethyl anisate, monoethyl phthalate, dimethyl phthalate, methyl ethyl phthalate, diethyl phthalate, di-n-propyl phthalate, diisopropyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-n-heptyl phthalate, di-n-octyl phthalate and diphenyl phthalate.

Examples of said sterically hindered amine include 2,6-substituted piperidines, 2,5-substituted pyrrolidines, and substituted methylenediamine compounds such as N,N,N',N'-tetramethylmethylenediamine.

Among these electron donors, alkoxysilane compounds represented by general formula R<sup>14</sup><sub>t</sub>Si(OR<sup>2</sup>)<sub>4-t</sub> give a particularly good result.

Concrete examples of such alkoxysilane compound include tetramethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, ethyltrimethoxysilane, phenyltrimethoxysilane, phenylmethyldimethoxysilane, tetraethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, phenyltriethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, butyltriethoxysilane, tetrabutoxysilane, vinyltributoxysilane and diethyldiethoxysilane.

The electron donor is used in an amount of 0.01 to 5 moles, preferably 0.03 to 3 moles, and particularly 0.05 to 1.0 mole, per one mole of the aluminum atom in the organoaluminum compound (B).

## (IV) Method of Polymerization

(1) The method for feeding the catalyst components into the polymerization reactor is not critical, so far as they are fed in a water-free state in an atmosphere of inert gas such as nitrogen or argon.

The solid catalyst component (A), organoaluminum compound (B) and the optionally used electron donor (C) may be fed either separately or after previously contacting two of them.

When crystalline polymers are produced, the following method is used.

The polymerization reaction can be carried out in a wide temperature range of -30°C to 200°C. However, if the temperature is lower than 0°C, the polymerization rate decreases, and at a temperature higher than 100°C a polymer having a high stereospecificity cannot be obtained. Thus, it is usually preferable to carry out the polymerization in the temperature range of 0 to 100°C. Though the pressure of polymerization is not critical, a pressure of 3 to 100 atmospheres is preferable from industrial and economical points of view. The polymerization can be effected by any of the continuous processes and batch processes. A slurry polymerization process using an inert hydrocarbon solvent such as propane, butane, pentane, hexane, heptane or octane, a liquid phase polymerization using no solvent, and a gas phase polymerization are also adoptable.

The alpha-olefins to which the present invention applies are those having 3 or more carbon atoms, of which concrete examples include propylene, butene-1, pentene-1, hexene-1, 3-methylpentene-1 and 4-methylpentene-1. However, the present invention is not limited by the compounds mentioned above. The polymerization of the present invention may be any homopolymerization and copolymerization, including the copolymerization with ethylene.

In carrying out the copolymerization, two or more species of olefins are mixed together and contacted mutually, whereby a copolymer of them can be obtained.

Further, a hetero-block copolymerization in which the polymerization is effected in two or more steps can also be carried out easily.

It is also possible to add a chain transfer agent such as hydrogen to control the molecular weight of the polymer.)

(2) Further, the invention provides a process for producing a granular elastomer which comprises carrying out a random copolymerization of ethylene and α-olefin in the gas phase by the use of the above-mentioned catalyst system and a process for producing a granular thermoplastic elastomer which comprises two steps substantially.

Hereunder, concrete embodiments of the polymerization will be mentioned.

In the production of a granular elastomer by a random copolymerization of ethylene and  $\alpha$ -olefin in the gas phase, the  $\alpha$ -olefins to be copolymerized with ethylene include propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1 and 3-methylbutene-1, among which propylene and butene-1 are particularly preferable.

In the copolymerization of the present invention, a polyene may additionally copolymerized with ethylene and  $\alpha$ -olefin to facilitate the vulcanization of the resulting copolymer. Concrete examples of said polyene include butadiene, dicyclopentadiene, 1,3,7-octatriene, vinylcyclohexane, 5-ethyldiene-2-norbornene, 5-isopropenyl-2-norbornene, 1,4-hexadiene, 1,5-hexadiene and 1,9-decadiene, among which nonconjugated dienes are preferable and straight chain nonconjugated dienes are particularly preferable.

The content of ethylene in the ethylene- $\alpha$ -olefin copolymer is 5 to 95% by weight and preferably 15 to 90% by weight. If the ethylene content in the formed copolymer exceeds the above-mentioned range, the rubbery character of the product is deteriorated. If its content is lower than the above-mentioned range, the low temperature characteristics and the rubbery character are deteriorated.

When the copolymerization is to be carried out in the presence of a polyene, the reaction is so controlled that the iodine number of the copolymer comes to 2 to 50 and preferably to 3 to 40.

In the present invention, the polymerization reaction can be advanced in two or more steps while changing the ethylene concentration. In such a case, it is also possible to carry out a homopolymerization of ethylene or  $\alpha$ -olefin to a small extent (for example, to an extent of 3% by weight or less based on the total quantity of polymer) in the first step.

Preferably, the polymerization is carried out at a temperature not higher than the temperature at which the polymer melts, preferably at 20 to 85°C and particularly at 40 to 75°C, at a pressure ranging from ordinary pressure to 40 bar (40 kg/cm<sup>2</sup>), under a condition not liquefying the monomer in the polymerization reactor. Preferably, hydrogen is added to the copolymerization system as a molecular weight regulator to control the melt-flow property, of the ultimate product. Further, an inert gas may be mixed into the gas mixture for polymerization. However, the use of too large an amount of inert gas (for example, an amount exceeding 25% by mole) is undesirable, because it markedly deteriorates the productivity of the process.

The molecular weight of the ethylene- $\alpha$ -olefin random copolymer formed by the polymerization reaction is 0.3 to 10, preferably 0.5 to 8, and particularly 1 to 5, as expressed by intrinsic viscosity  $[\eta]$  measured in tetralin at 135°C. If  $[\eta]$  is too low, no sufficient tensile strength can be achieved.

In the present invention, it is also possible to produce a granular thermoplastic elastomer by a process comprising substantially two steps by carrying out a homopolymerization (hereinafter referred to as "step 1") of propylene or ethylene prior to the above-mentioned gas phase random copolymerization of ethylene and  $\alpha$ -olefin.

When homopolymerization of propylene is carried out in step 1, the step 1 is carried out in liquefied propylene and/or the gas phase. The effect of the invention can be achieved by any of the methods which comprise effecting the polymerization in liquefied propylene, the method which comprises effecting the polymerization in liquefied propylene and then effecting the polymerization in gas phase and the method which comprises effecting the polymerization in gas phase.

Next, in case that propylene is homopolymerized in step 1, the embodiment of polymerization of step 1 is as follows.

The polymerization is carried out by polymerizing propylene itself and it is also possible to copolymerize propylene with a comonomer which is ethylene or  $\alpha$ -olefin having 4 to 6 carbon atoms. In this case, the amount of the comonomer should be so controlled that the comonomer content in the resulting copolymer comes to preferably 6% by mole or below and most preferably 4% by mole or below.

When the polymerization is carried out in liquefied propylene, it is preferably carried out at a temperature of 40°C to 90°C at a pressure of 17 to 50 bar (17 to 50 kg/cm<sup>2</sup>). On the other hand, when the polymerization is carried out in the gas phase, the polymerization is carried out at a temperature not higher than the melting temperature of the polymer and preferably in the temperature range of 40°C to 100°C, at a pressure ranging from ordinary pressure 40 bar (40 kg/cm<sup>2</sup>), under a condition not liquefying the monomer in the polymerization reactor. Further, in this process, the polymerization is carried out preferably in the presence of a molecular weight regulator such as hydrogen or the like to improve the melt flow property of the ultimate product.

When homopolymerization of ethylene is carried out in step 1, the step 1 is carried out in the form of a slurry polymerization in propane solvent or butane solvent or in the form of gas phase polymerization of ethylene.

A more concrete embodiment of the polymerization of step 1 of this case will be mentioned below.

The polymerization of step 1 involves not only a homopolymerization of ethylene but also a copolymerization of ethylene and a small quantity of  $\alpha$ -olefin having 3 to 6 carbon atoms as a comonomer. In this case, the amount of the comonomer should be so controlled that the content of the comonomer in the resulting copolymer comes to preferably 6% by mole or below and more preferably 4% by mole or below.

When the polymerization is carried out in propane solvent or butane solvent, it is preferably carried out at a temperature of 40°C to 95°C at a pressure of 17 to 50 bar (17 to 50 kg/cm<sup>2</sup>). On the other hand, when the polymerization is carried out in gas phase, it is carried out at a temperature not higher than the melting temperature of the polymer and preferably at a temperature of 40°C to 110°C, at a pressure ranging from ordinary pressure to 50 bar (50 kg/cm<sup>2</sup>), under a condition not liquefying the monomer in the polymerization reactor. Further, in this process, it is preferable to carry out the polymerization in the presence of a molecular weight regulator such as hydrogen to improve the melt flow property of the ultimate product.

In any of these cases, step 2 of the polymerization is carried out in succession to step 1. That is, a random copolymerization of ethylene and  $\alpha$ -olefin is carried out in gas phase. Its details are as those mentioned above.

The copolymer formed in step 2 of the invention occupies 60 to 97% by weight, preferably 70 to 95% by weight and particularly 75 to 90% by weight of the total quantity of the polymers. A higher formation of polymer in step 2 gives a product richer in rubbery character, and a lower formation of polymer in step 2 gives a product exhibiting a more plastic behavior.

By carrying out the polymerization process of the invention, a granular thermoplastic elastomer and a granular elastomer having good particle characteristics are obtained, and their adhesive force is usually 59 N/cm<sup>2</sup> (6.0 g/cm<sup>2</sup>) or below.

The gas phase polymerization reactor used for carrying out the present invention is not critical, but any of the known stirring-mixing tank type reactor, fluidized bed type reactor, fluidized bed type reactor equipped with a stirrer may be used.

The polymerization reaction of the invention can be carried out by any of the continuous process using in-series combined two or more reactors, the batch polymerization process in one or more reactors, and combination of the above-mentioned two processes.

Next, the process of the present invention will be illustrated in more detail with reference to the following non-limiting examples.

The physical data referred to in these examples were measured according to the following methods.

Intrinsic Viscosity (hereinafter simply referred to as  $[\eta]$ ):

Measured in tetralin solvent at 135°C.

$[\eta]_E, [\eta]_P$  ----- Intrinsic viscosities of the polymers formed in step 1,

$[\eta]_T$  ----- Intrinsic viscosity of total polymer,

$[\eta]_{EP}$  ----- Intrinsic viscosity of the polymer formed in step 2.

$[\eta]_{EP}$  was calculated according to the following equation:

$$[\eta]_{EP} = \frac{[\eta]_T - [\eta]_E(E)}{(EP)} \quad \text{or} \quad \frac{[\eta]_T - [\eta]_P(P)}{(EP)}$$

where (E) and (P) each represents the proportion of the quantity of the polymers in step 1 (weight fraction) and (EP) represents the proportion of the quantity of the polymers in step 2 (weight fraction).

Contents of Ethylene and 1,9-Decadiene:

By infrared spectroscopic measurement, ethylene was determined from the adsorption bands of 722, 733 and 736 cm<sup>-1</sup>, and 1,9-decadiene was determined from the absorption band of 1640 cm<sup>-1</sup>. The ethylene content thus determined roughly coincided with the value determined from material balance.

Adhesive Force of Polymer Particle:

Two cells for shearing test, made of aluminum plate, 30 mm in width, 53 mm in length and 12 mm in height, were tightly superposed up-and-down, and the polymer particles to be tested were introduced therein. After a preliminary pressing under a load of 1,000 g for 30 seconds, one surface shearing test was

carried out at ordinary temperature at a drawing speed of 100 mm/minute under a vertical load of 50 g, 100 g, 200 g, 300 g or 400 g to measure the shearing stress at each vertical load. The plot of shearing stress against vertical load was approximated to linearity by the least square method, and the shearing stress extrapolated to zero gram vertical load was taken as the adhesive force.

20 °C. Xylene-soluble Fraction (hereinafter simply referred to as CXS):

One gram of polymer was dissolved into 200 ml of boiling xylene, slowly cooled to 50 °C, then cooled to 20 °C with stirring while dipping it in ice water, allowed to stand at 20 °C for 3 hours and then filtered to remove the deposited polymer. Xylene was evaporated off from the filtrate and the residue was dried in vacuum at 60 °C and the polymer soluble in xylene at 20 °C was recovered.

Pore Volume:

Pore volume was measured in the pore radius range of 40 to 75,000 • 10<sup>-10</sup> (40 to 75,000 Å) by the mercury injection method using Poresizer 9310 (porosimeter) manufactured by Micromeritics Co.

Mean Particle Diameter of Solid Catalyst:

It was determined by optical microscopic measurement.

#### Example 1

##### (A) Synthesis of Organomagnesium Compound

After replacing the inner atmosphere of a flask having an inner volume of 1 liter and equipped with a stirrer, a reflux condenser, a dropping funnel and a thermometer with argon gas, 32.0 g of sliced metallic magnesium was thrown into the flask.

Into the dropping funnel 120 g of n-butyl chloride and 500 ml of di-n-butyl ether, were charged, and about 30 ml of the mixture was dropped onto the magnesium in the flask to start the reaction. After the start of the reaction, the mixture in the dropping funnel was continuously dropped to 50 °C over a period of 4 hours, after which the reaction was continued for an additional one hour at 60 °C. Then, the reaction mixture was cooled to room temperature, and the solid matter was filtered off.

The n-butylmagnesium chloride in the di-n-butyl ether was hydrolyzed with 1 N sulfuric acid and back-titrated with 1 N aqueous solution of sodium hydroxide, using phenolphthalein as an indicator. Thus, it was found that the concentration of n-butylmagnesium chloride was 2.0 M/liter.

##### (B) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 20 ml of n-butyl ether and 5.0 g of porous polymer beads of a styrene-divinylbenzene copolymer (Chromosorb 101®, manufactured by Johns-Manville Co.) were thrown into the flask. The polymer beads had a pore volume (hereinafter referred to as "dVp") of 0.92 ml/g as measured in the pore radius range of 100 to 5000 • 10<sup>-10</sup> m (100 to 5,000 Å) by means of porosimeter, and the beads were previously vacuum-dried at 80 °C for 0.5 hour and then put to use. While stirring the content of the flask, 14.0 g of the organomagnesium compound synthesized in (A) was dropped from the dropping funnel over a period of 10 minutes while keeping the inner temperature of the flask at 80 °C. Thereafter, the content of the flask was reacted for an additional one hour at that temperature. After washing the product twice with each 20 ml portions of n-butyl ether and twice with each 20 ml portions of n-heptane, it was dried under reduced pressure to obtain 5.0 g of an organomagnesium-treated product.

After replacing the inner atmosphere of a flask having an inner volume of 100 ml and equipped with a stirrer and a dropping funnel with argon gas, 5.0 g of the organomagnesium-treated product synthesized above was thrown into the flask together with 25 ml of n-heptane, 0.44 g (1.3 millimoles) of tetrabutoxytitanium and 4.5 g (21.6 millimoles) of tetraethoxysilane and the content of the flask was stirred at 30 °C for 30 minutes.

Next, 4.6 ml of the organomagnesium compound synthesized in (A) was dropped from the dropping funnel over a period of one hour while keeping the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for one hour and then at room temperature for one hour, after

which it was washed thrice with each 25 ml portions of n-heptane and dried under reduced pressure to obtain 6.2 g of a brown-colored solid product.

The solid product thus obtained contained 0.4% by weight of titanium atoms and 3.9% by weight of magnesium atoms.

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#### (C) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 6.0 g of the solid product synthesized in the reduction (B), 30.0 g of monochlorobenzene and 0.41 ml (1.5 millimoles) of diisobutyl phthalate were introduced into the flask and reacted at 80 °C for one hour.

The solid product was separated from the liquid phase at 80 °C and washed twice with each 30 ml portions of n-heptane.

After washing it, 30.0 ml of monochlorobenzene, 0.53 ml (3.1 millimoles) of n-butyl ether and 9.6 ml (87.3 millimoles) of titanium tetrachloride were added to the content of the flask and reacted at 80 °C for 3 hours. After the reaction, the solid product was separated from the liquid phase and washed twice with each 30 milliliter portions of monochlorobenzene at that temperature. The above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was repeated over a period of one hour, and the treated product was washed twice with each 30 ml portions of n-heptane and then dried under reduced pressure to obtain 5.4 g of a brown-colored solid catalyst component.

The solid catalyst component contained 0.5% by weight of titanium atoms, 4.3% by weight of magnesium atoms and 0.7% by weight of phthalic ester.

The solid catalyst component obtained herein had a mean particle diameter of 200  $\mu\text{m}$  and dVp (pore volume) of 0.75 ml/g.

#### (D) Polymerization

Using an autoclave having an inner volume of 5 liters and equipped with a stirrer, a homopolymerization of propylene was carried out in step 1 and a random polymerization of ethylene and propylene was carried out in step 2.

After drying the autoclave at 80 °C for one hour and evacuating it with a vacuum pump, 0.5 g of triethylaluminum, 0.13 g of phenyltrimethoxysilane and 564.0 mg of the solid catalyst component prepared in (C) were charged, and hydrogen was introduced until its partial pressure came to 0.52 bar (0.53 kg/cm<sup>2</sup>).

Next, 1.3 kg of liquefied propylene was introduced into the autoclave under pressure, and the temperature was elevated to 75 °C. After carrying out a homopolymerization of propylene at 75 °C for 15 minutes, the unreacted monomer was purged and a small amount of polymer was sampled to measure  $[\eta]_p$  and CXS. Then 0.074 bar (0.075 kg/cm<sup>2</sup>) of hydrogen was charged, and pressure was elevated up to 9 bar (8 kg/cm<sup>2</sup> G) with propylene, after which pressure was further elevated to 11 bar (10 kg/cm<sup>2</sup> G) with ethylene. Then, the temperature was adjusted to 70 °C and the polymerization of step 2 was started.

While feeding the ethylene/propylene gaseous mixture (50%/50% by volume) so as to maintain a total pressure of 10 bar (10 kg/cm<sup>2</sup>), a copolymerization of ethylene and propylene was carried out in the gas phase for 420 minutes.

After completion of the polymerization, the unreacted monomer was purged and 643 g of a granular thermoplastic elastomer having good particle characteristics were obtained. It contained neither fine powders nor coarse particles.

After opening the autoclave, its inside was examined. No deposition of polymer was found at all on the inner wall nor on the stirrer.

Formation of total polymer per one gram titanium atom in the solid catalyst component (hereinafter referred to as PP/Ti) was 228,000 (g/g). In the propylene homopolymer formed in step 1 (hereinafter referred to as P), CXS was 3.8% by weight.

In the total polymer, the content of the ethylene/propylene copolymer formed in step 2 (hereinafter referred to as EP) was 85% by weight. In the EP, the content of ethylene was 48% by weight. Molecular weights of the polymers were as follows:

$[\eta]_p = 1.7$ ,  $[\eta]_{EP} = 3.8$ ,  $[\eta]_T = 3.5$ .

Adhesive force of the polymer particle obtained herein was 2.8 g/cm<sup>2</sup>.

Conditions and results of the polymerization are summarized in Table 1 and Table 2, respectively.

## Comparative Example 1

## (A) Synthesis of Solid Product

5 After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 15.0 g of Supermicro Beads Silica Gel ID type manufactured by Fuji Devlson Kagaku K.K. ( $dVp = 0.84 \text{ ml/g}$ ) which had been vacuum-dried at  $100^\circ\text{C}$  for 2 hours were thrown into the flask together with 46 ml of n-butyl ether. While stirring them, 42.0 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of 10 minutes while keeping the inner temperature of the flask at  $30^\circ\text{C}$ . Thereafter, the content of the flask was reacted at that temperature for an additional 2 hours. The product was washed twice with each 20 ml portions of n-butyl ether and twice with each 40 ml portions of n-heptane and then dried under reduced pressure to obtain 14.8 g of organomagnesium-treated silica gel.

15 After replacing the inner atmosphere of a flask having an inner volume of 300 ml and equipped with a stirrer and a dropping funnel with argon gas, 13.8 g of the organomagnesium-treated silica gel obtained above, 69 ml of n-heptane, 0.77 g (2.3 millimoles) of tetrabutoxytitanium and 8.04 g (38.6 millimoles) of tetraethoxysilane were charged into the flask and stirred at  $30^\circ\text{C}$  for 30 minutes.

20 Then, 22.6 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of one hour while keeping the inner temperature of the flask at  $5^\circ\text{C}$ . After dropping it, the content of the flask was stirred at  $5^\circ\text{C}$  for one hour and then at room temperature for one hour, after which the product was washed thrice with each 60 ml portions of n-heptane and dried under reduced pressure to obtain 21.1 g of a brown-colored solid product.

The solid product thus obtained contained 0.5% by weight of titanium atoms and 5.9% by weight of magnesium atoms.

## (B) Synthesis of Solid Catalyst Component

30 After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 5.6 g of the solid product synthesized in the reduction of (A), 18.8 ml of toluene and 0.74 ml (2.8 millimoles) of diisobutyl phthalate were charged and reacted at  $95^\circ\text{C}$  for one hour.

After the reaction, the solid product was separated from the liquid phase and washed twice with each 20 ml portions of toluene.

35 After washing it, 18.8 ml of toluene, 0.65 ml (3.8 millimoles) of n-butyl ether and 11.4 ml (104 millimoles) of titanium tetrachloride were added and reacted at  $95^\circ\text{C}$  for 3 hours. After the reaction, the solid product was separated from the liquid phase at  $95^\circ\text{C}$  and washed at that temperature twice with each 20 ml portions of toluene. Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour and the product was washed twice with each 20 ml portions of n-heptane, after which it was dried under reduced pressure. Thus, 4.8 g of a brown-colored solid catalyst component was obtained.

40 The solid catalyst component contained 1.1% by weight of titanium atoms, 7.8% by weight of magnesium atoms and 1.5% by weight of phthalic ester.

This solid catalyst component had a mean particle diameter of  $40 \mu\text{m}$ , and  $dVp$  (pore volume) of  $0.35 \text{ ml/g}$ .

## (C) Polymerization

45 Using 297.0 mg of the solid catalyst component obtained in (B), a block copolymerization of P-EP was carried out under the same conditions as in Example 1 (D). Conditions and results of the polymerization are shown in Table 1 and Table 2, respectively.

50 Since in this experiment silica gel was used as the catalyst carrier instead of organic porous polymer, the resulting polymer was agglomerated. Its particle characteristics were extremely bad, and its adhesive force was  $7.7 \text{ g/cm}^2$ .

Conditions and results of the polymerization are shown in Table 1 and Table 2, respectively, together with those of Comparative Examples 2 to 4.

## Comparative Example 2

## (A) Synthesis of Solid Product

5 After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 8.25 g of silica gel (grade 952, manufactured by Fuji Devision Kagaku K.K.) which had been calcined at 800°C for 8 hours in an atmosphere of nitrogen ( $dV_p = 0.88$  ml/g) was charged into the flask together with 41.3 ml of n-heptane, 1.12 g (3.3 millimoles) of tetrabutoxytitanium and 11.8 g (56.7 millimoles) of tetraethoxysilane, and the content of the flask was stirred at room  
10 temperature for 30 minutes.

Then, 30.0 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of one hour, while keeping the inner temperature of the flask at 5°C. After dropping it, the resulting mixture was stirred at 5°C for 30 minutes and then at 30°C for one hour, after which the product was washed twice with each 40 ml portions of n-heptane and dried under reduced  
15 pressure to obtain 17.5 g of a brown-colored solid product.

## (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 4.5 g  
20 of the solid product, 15.1 ml of toluene and 1.67 ml (6.2 millimoles) of diisobutyl phthalate were added and reacted at 95°C for one hour.

After the reaction, the solid product was separated from the liquid phase and washed twice with each 15 ml portions of toluene.

After washing it, 15.1 ml of toluene, 1.0 ml (5.7 millimoles) of n-butyl ether and 17.7 ml (161 millimoles)  
25 of titanium tetrachloride were added to the flask and reacted at 95°C for 3 hours. After the reaction, the solid was separated from the liquid phase at 95°C, and washed at that temperature twice with each 15 ml portions of toluene. Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was repeated over a period of one hour and the product was washed twice with each 15 ml portions of n-heptane, after which it was dried under reduced pressure to obtain 3.6 g of a brown-colored  
30 solid catalyst component.

The solid catalyst component thus obtained contained 1.9% by weight of titanium atoms 9.0% by weight of magnesium atoms and 2.3% by weight of phthalic ester. Its pore volume  $dV_p$  was 0.25 ml/g.

## (C) Polymerization

35 Using 103.2 mg of the solid catalyst component synthesized in (B), a block copolymerization of P-EP was carried out under the same conditions as in Example 1 (D).

Since in this experiment silica gel was used instead of organic porous polymer as the carrier for the catalyst, the resulting polymer was agglomerated. Its particle characteristics were extremely bad, and its  
40 adhesive force was 82 N/cm<sup>2</sup> (8.4 g/cm<sup>2</sup>).

## Comparative Example 3

## (A) Synthesis of Solid Product

45 After replacing the inner atmosphere of a flask having an inner volume of 500 ml and equipped with a stirrer and a dropping funnel with argon gas, 150 ml of n-heptane, 7.6 g (22.4 millimoles) of tetrabutoxytitanium and 78 g (378 millimoles) of tetraethoxysilane were added to form a uniform solution. Then, 182 ml of the organomagnesium compound synthesized in Example 1 (A) was slowly dropped thereinto over a  
50 period of 3 hours from the dropping funnel while keeping the inner temperature of the flask at 5°C. After dropping it, the mixture was stirred at room temperature for an additional one hour and the solid was separated from the liquid phase, washed thrice with each 300 ml portions of n-heptane and dried under reduced pressure to obtain 62.0 g of a brown colored solid product.

## 55 (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 200 ml with argon gas, 15 g of the solid product synthesized in (A), 75 ml of toluene and 8.1 ml of diisobutyl phthalate were added and

reacted at 95 °C for one hour.

After the reaction, the solid was separated from liquid phase and washed thrice with each 75 ml portions of n-heptane.

Then, 38 ml of toluene, 5.0 ml (88.5 millimoles) of n-butyl ether and 88.5 ml (807 millimoles) of titanium tetrachloride were added and reacted at 95 °C for 3 hours.

After the reaction, the solid was separated from liquid phase and washed twice at 95 °C with each 75 ml portions of toluene.

Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, and the product was washed twice with each 75 ml portions of n-heptane and dried under reduced pressure to obtain 13 g of a loess-colored solid catalyst component.

This solid catalyst component contained 1.9% by weight of titanium atoms 19.4% by weight of magnesium atoms and 5.0% by weight of phthalic ester. Its mean particle diameter was 35 μm, and its pore volume dVp was 0.27 ml/g.

#### 15 (C) Polymerization

Using 31.8 mg of the solid catalyst component synthesized in (B), a block copolymerization of P-EP was carried out under the same conditions as in Example 1 (D). Conditions and results of the polymerization are shown in Table 1 and Table 2, respectively.

Since in this experiment the solid catalyst component was not impregnated in a porous carrier, the particle characteristics were extremely bad, in spite of the considerably great pore volume. Thus, examination of the opened autoclave revealed that polymer particles were deposited on the inner wall of the autoclave to form a almost solidified layer.

#### 25 Comparative Example 4

##### (A) Synthesis of Solid Catalyst Component

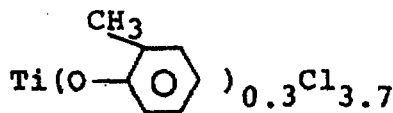
A solid catalyst component was synthesized by the same procedure as mentioned in Example 5 of Japanese Patent Application Kokai (Laid-Open) No. 61-287,917 (USP 4,412,049).

Thus, after replacing the inner atmosphere of a flask having an inner volume of 300 ml and equipped with a stirrer and a dropping funnel with argon gas, 57.2 ml of the organoaluminum compound synthesized in Example 1 (A) was added. While keeping the inner temperature of the flask at 20 °C, 12.8 ml of silicon tetrachloride was slowly dropped into a solution of n-butylmagnesium chloride in n-butyl ether over a period of one hour. After dropping it, the mixture was stirred at 20 °C for an additional one hour, and the reaction mixture was filtered and the solid product was washed 4-times with each 100 ml portions of hexane to obtain a carrier.

Then, 70 ml of hexane was added to prepare a slurry and the inner temperature was kept at 60 °C.

Then, a solution of 4.2 g of phenol in 100 ml of hexane and 6.4 ml of ethyl benzoate were added and reacted at 60 °C for 30 minutes. The reaction mixture was filtered and the solid product was washed thrice with each 150 ml portions of hexane at 60 °C.

Then, 80 ml of monochlorobenzene was added to prepare a slurry, after which a solution composed of 122.4 g of



50 and 48 ml of monochlorobenzene was added and reacted at 100 °C for 30 minutes. After the reaction, the reaction mixture was filtered at 100 °C and the solid was washed with 150 ml of toluene and then thrice with each 100 ml portions of hexane and dried to obtain 15.1 g of a solid catalyst component.

This solid catalyst component contained 2.5% by weight of titanium atoms, 20.9% by weight of magnesium atoms, 1.7% by weight of phenol and 9.1% by weight of ethyl benzoate. This solid catalyst component had a mean particle diameter of 30 μm, and its pore volume dVp was 0.29 ml/g.

## (B) Polymerization

A block copolymerization of P-EP was carried out in the same manner as in Example 1 (D), except that 32.4 mg of the solid catalyst component synthesized in (A) was used and the phenyltrimethoxysilane used in Example 1 as electron donor (C) was replaced with 0.2 g of methyl p-toluate.

The conditions and results of the polymerization are shown in Table 1 and Table 2, respectively. In this experiment, the catalyst activity changed greatly with time and the activity was completely lost in the course of random copolymerization of ethylene and propylene of step 2, so that no thermoplastic elastomer having the composition of the present invention was obtained.

## Example 2

Using the solid catalyst component synthesized in Example 1, a block copolymerization of P-EP was carried out.

After drying an autoclave at 80°C for one hour and evacuating it with a vacuum pump, 0.5 g of triethylaluminum, 0.13 g of phenyltrimethoxysilane and 282.9 mg of a solid catalyst component prepared in Example 1 were charged, and then hydrogen was charged until its partial pressure reached 0.52 bar (0.53 kg/cm<sup>2</sup>).

Then, 1.3 kg of liquefied propylene was introduced into the autoclave under a pressure and heated to 75°C. After carrying out a homopolymerization of propylene at 75°C for 10 minutes, the unreacted monomer was purged and a small amount of polymer was sampled to measure  $[\eta]_p$  and CXS. Then, 0.3 bar (0.3 kg/cm<sup>2</sup>) of hydrogen was fed, and the pressure was elevated to 5 bar (4 kg/cm<sup>2</sup> G) with propylene and further was elevated to 11 bar (10 kg/cm<sup>2</sup> G) with ethylene, after which the temperature was adjusted to 70°C and the polymerization of step 2 was started.

While feeding the ethylene/propylene gaseous mixture (80%/20% by volume) so as to maintain a total pressure of 11 bar (10 kg/cm<sup>2</sup> G), an ethylene/propylene copolymerization was carried out in the gas phase for a period of 540 minutes.

After completion of the polymerization, the unreacted monomer was purged and 368 g of a granular thermoplastic elastomer having good powder characteristics were obtained. It contained no fine powders nor coarse particles.

After opening the autoclave its inside was examined to reveal that no polymer was deposited at all on the inner wall of autoclave nor on the stirrer.

Conditions and results of the polymerization are shown in Table 1 and Table 2, respectively.

## Example 3

A block copolymerization of P-EP was carried out under the same conditions as in Example 1 (D), except that 377.0 mg of the solid catalyst component synthesized in Example 1 were used and 0.2 bar (0.2 kg/cm<sup>2</sup>) of hydrogen was charged in step 2 of the polymerization. Conditions and results of the polymerization are shown in Table 1 and Table 2, respectively.

## Example 4

Using the solid catalyst component synthesized in Example 1, a homopolymerization of propylene was carried out in step 1 and random copolymerization of ethylene and butene-1 was carried out in step 2.

After drying the autoclave at 80°C for one hour and evacuating it with a vacuum pump, 0.5 g of triethylaluminum, 0.13 g of phenyltrimethoxysilane and 372.4 mg of the solid catalyst component synthesized in Example 1 were charged, and hydrogen was fed until its partial pressure reached 0.52 bar (0.53 kg/cm<sup>2</sup>).

Then, 1.3 kg of liquefied propylene was fed into the autoclave under elevated pressure and heated to 75°C. After carrying out a homopolymerization of propylene at 75°C for 10 minutes, the unreacted monomer was purged and a small amount of polymer was sampled out to measure  $[\eta]_p$  and CXS. Then, 0.074 bar (0.075 kg/cm<sup>2</sup>) of hydrogen was fed and an ethylene/butene-1 gaseous mixture (80%/20% by volume) was fed to maintain a total pressure of 4 bar (4 kg/cm<sup>2</sup>), and a copolymerization of ethylene and butene-1 was carried out in the gas phase at 75°C for 420 minutes. After completion of the polymerization, the unreacted monomer was purged, and 260 g of a thermoplastic elastomer having good particle characteristics were obtained.

After opening the autoclave, its inside was examined to reveal that no polymer was deposited at all on the inner wall of the autoclave nor on the stirrer.

The formation of total polymer per 1 g of titanium atom (PP/Ti) was 140,000. The total polymer contained 73% by weight of the ethylene/butene-1 copolymer formed in step 2 (hereinafter referred to as EB). In EB, the content of ethylene was 77% by weight.

The molecular weights were as follows:  $[\eta]_P = 2.2$ ,  $[\eta]_{EB} = 4.1$ ,  $[\eta]_T = 3.6$ . The polymer thus obtained had an adhesive force of 24 N/cm<sup>2</sup> (2.4 g/cm<sup>2</sup>).

#### Example 5

##### (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 7.0 g of Chromosrob 101® which had been vacuum-dried at 80 °C for one hour and 28 ml of n-butyl ether were charged into the flask. While stirring the content of the flask, 20.0 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of 30 minutes during which the inner temperature of the flask was maintained at 80 °C. After reacting the content of the flask at that temperature for an additional one hour, the product was washed twice with each 20 ml portions of n-butyl ether and twice with each 20 ml portions of n-heptane and dried under reduced pressure to obtain 7.0 g of an organomagnesium-treated product. Then, after replacing the inner atmosphere of a flask having an inner volume of 100 ml and equipped with a stirrer and a dropping funnel with argon gas, 7.0 g of the organoaluminum-treated product synthesized above were added to the flask together with 35 ml of n-heptane, 0.62 g (1.8 millimoles) of tetrabutoxytitanium and 6.31 g (30.2 millimoles) of tetraethoxysilane, and content of the flask was stirred at 30 °C for 30 minutes.

Then, 16.0 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel while maintaining the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for one hour and then at room temperature for one hour, and the product was washed thrice with each 30 ml portions of n-heptane and dried under reduced pressure to obtain 11.6 g of a brown colored solid product.

##### (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 4.14 g of the solid product, 13.8 ml of toluene, 0.91 ml (5.4 millimoles) of n-butyl ether and 16.1 ml (146 millimoles) of titanium tetrachloride were added and reacted at 95 °C for 3 hours. After the reaction, the solid was separated from the liquid phase at 95 °C and washed twice at that temperature with each 20.0 ml portions of toluene. The above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, and the product was washed twice with each 20.0 ml portions of n-heptane, after which it was dried under reduced pressure to obtain 3.53 g of a brown colored solid catalyst component.

The solid catalyst component contained 1.6% by weight of titanium atoms and 6.3% by weight of magnesium atoms. It had a mean particle diameter of 200 μm and a pore volume dVp of 0.53 ml/g.

##### (C) Polymerization

Using an autoclave having an inner volume of 5 liters and equipped with a stirrer, a homopolymerization of ethylene was carried out in step 1 and a random copolymerization of ethylene and propylene was carried out in step 2.

After drying the autoclave at 80 °C for one hour, 800 g of butane was charged and heated to 60 °C. Then, hydrogen was charged until its partial pressure reached 4 bar (3 kg/cm<sup>2</sup> G) and then ethylene was fed up to a pressure of 21 bar (20 kg/cm<sup>2</sup> G) and then 0.5 g of triethylaluminum, 0.13 g of phenyltrimethoxysilane and 313.2 mg of the solid catalyst component prepared in (B) were introduced under pressure into the autoclave together with a small amount of n-heptane. A homopolymerization of ethylene was carried out for 50 minutes while maintaining a total pressure of 21 bar (20 kg/cm<sup>2</sup> G) and a temperature of 60 °C, after which the unreacted monomer and butane were purged and a small amount of polymer was sampled to measure  $[\eta]_E$ . Then, 1.074 bar (0.075 kg/cm<sup>2</sup> G) of hydrogen was fed and the pressure was elevated to 9 bar (8 kg/cm<sup>2</sup> G) with propylene and then to 11 bar (10 kg/cm<sup>2</sup> G) with ethylene, after which temperature was adjusted to 70 °C and the polymerization of step 2 was started.

While feeding an ethylene/propylene gaseous mixture (50%/50% by volume) so as to maintain a total pressure of 11 bar (10 kg/cm<sup>2</sup> G), an ethylene/propylene copolymerization reaction was carried out in the gas phase for 90 minutes. After completion of the polymerization, the unreacted monomer was purged, and 338 g of a granular thermoplastic elastomer having good powder characteristics were obtained. It was free from fine powder and coarse particles. After opening the autoclave, its inside was examined to reveal that no polymer was deposited at all on the inner wall of the autoclave and the stirrer.

The formation of total polymer per 1 g of solid catalyst (hereinafter referred to as P/cat (g/g)) was 1.080.

The homopolymer formed in step 1 (hereinafter referred to as E) had an intrinsic viscosity  $[\eta]_E$  of 1.7. The total polymer contained 85% by weight of the ethylene/propylene copolymer formed in step 2 (hereinafter referred to as EP). The content of ethylene in EP was 48% by weight, and intrinsic viscosities of total polymer and EP here as follows:  $[\eta]_T = 2.9$ ,  $[\eta]_{EP} = 3.1$ . Adhesive force of the polymer particle obtained herein was 4.2 g/cm<sup>2</sup>.

#### Comparative Example 5

##### (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 500 ml and equipped with a stirrer and a dropping funnel with argon gas, 150 ml of n-heptane, 7.6 g (22.4 millimoles) of tetrabutoxytitanium and 78 g (378 millimoles) of tetraethoxysilane were added to form a uniform solution. Then, 182 ml (400 millimoles) of the organomagnesium compound synthesized in Example 1 (A) were slowly dropped from the dropping funnel over a period of 3 hours, while keeping the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at room temperature for an additional one hour, and the solid product was separated from the liquid phase at room temperature, washed thrice with each 300 ml portions of n-heptane and dried under reduced pressure. Thus, 62.0 g of a brown colored solid product were obtained.

##### (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 10.7 g of the solid product obtained in (A), 35.6 ml of toluene, 2.36 g (13.9 millimoles) of n-butyl ether and 41.6 ml (378 millimoles) of titanium tetrachloride were added and reacted at 95 °C for 3 hours. After the reaction, the solid was separated from the liquid phase at 95 °C and washed at that temperature twice with each 35 ml portions of toluene.

Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour and the product was washed twice with each 35 ml portions of n-heptane, after which it was dried under reduced pressure to obtain 9.8 g of a loess-colored solid catalyst component.

The solid catalyst component contained 7.6% by weight of titanium atoms and 18.5% by weight of magnesium atoms. Its mean particle diameter was 35  $\mu$ m, and its pore volume dVp was 0.17 ml/g.

##### (C) Polymerization

Using 127.0 mg of the solid catalyst component synthesized in (B), a block copolymerization of E-EP was carried out under the same conditions as in Example 5 (C). Conditions and results of the polymerization are shown in Table 3 and Table 4, respectively.

Since in this experiment the solid catalyst component was not impregnated in a porous carrier, the particle characteristics were extremely bad. That is, examination of the inside of the opened autoclave revealed that polymer particles were deposited on the inner wall of the autoclave to form almost solidified layers.

#### Comparative Example 6

##### (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 10.2 g of Supermicro Beads Silica Gel type 4B (manufactured by Fuji Davison Kagaku K.K., dVp = 0.15 ml/g) which had been calcined at 700 °C for 8 hours in an

atmosphere of nitrogen were charged together with 51.0 ml of n-heptane, 0.47 g (1.4 millimoles) of tetrabutoxytitanium and 5.20 g (23.2 millimoles) of tetraethoxysilane and the content of the flask was stirred at 30 °C for 45 minutes.

Then, 12.4 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of 45 minutes, while keeping the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for 45 minutes and then at 30 °C for 45 minutes, and then the product was washed twice with each 51.0 ml portions of n-heptane and dried under reduced pressure to obtain 13.8 g of a brown colored solid product.

#### (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 6.22 g of the solid product prepared in (A), 20.7 ml of toluene, 1.37 ml (8.1 millimoles) of n-butyl ether and 24.2 ml (220 millimoles) of titanium tetrachloride were added and reacted at 95 °C for 3 hours. After the reaction, the solid was separated from the liquid phase at 95 °C and washed at that temperature twice with each 20.7 ml portions of toluene. The above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour and the product was washed twice with each 20.7 ml portions of n-heptane, after which it was dried under reduced pressure to obtain 5.8 g of a brown colored solid catalyst component.

The solid catalyst component thus obtained contained 2.1% by weight of titanium atoms and 3.5% by weight of magnesium atoms. Its mean particle diameter was 40 µm, provided that this solid catalyst component contained a considerable amount of fine powders. Its pore volume dVp was as small as 0.07 ml/g.

#### (C) Polymerization

Using 359.0 mg of the solid catalyst component synthesized in (B), a block copolymerization of E-EP was carried out under the same conditions as in Example 5 (C).

The conditions and results of the polymerization are shown in Table 3 and Table 4, respectively. Since in this experiment the solid catalyst component had an extremely small pore volume, particle characteristics of the resulting polymer were very bad. Thus, examination of the opened autoclave revealed that polymer particles were deposited on the inner wall of the autoclave to form almost solidified layers.

### Example 6

#### (A) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 4.96 g of the solid product prepared by the reduction of Example 5 (A), 16.5 ml of toluene and 1.26 ml (4.7 millimoles) of diisobutyl phthalate were added and reacted at 95 °C for one hour.

The solid was separated from liquid phase and washed twice with each 16.5 ml portions of toluene.

After washing it, 16.5 ml of toluene, 1.1 ml (6.4 millimoles) of n-butyl ether and 19.3 ml (176 millimoles) of titanium tetrachloride were added to the flask and reacted at 95 °C for 3 hours. After the reaction, the solid was separated from the liquid phase at 95 °C and washed at that temperature twice with each 16.5 ml portions of toluene. The above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, and then the product was washed twice with each 16.5 ml portions of n-heptane, after which it was dried under reduced pressure to obtain 3.90 g of a brown colored solid catalyst component.

The solid catalyst component thus obtained contained 0.5% by weight of titanium atoms, 4.3% by weight of magnesium atoms and 0.7% by weight of phthalic ester.

Its mean particle diameter was 200 µm, and its pore volume dVp was 0.75 ml/g.

#### (B) Polymerization

Using 421.3 mg of the solid catalyst component synthesized in (A), a block copolymerization of E-EP was carried out under the same conditions as in Example 5 (C). Conditions and results of the polymerization are shown in Table 3 and Table 4, respectively.

## Example 7

## (A) Polymerization

Using an autoclave having an inner volume of 5 liters and equipped with a stirrer, a homopolymerization of ethylene was carried out in step 1 and a random copolymerization of ethylene and propylene was carried out in step 2.

After drying the autoclave at 80 °C for one hour, 800 g of butane was fed and the temperature was elevated to 60 °C. Then, hydrogen was fed until its partial pressure reached 4 bar (3 kg/cm<sup>2</sup> G), and then the pressure was elevated to 21 bar (20 kg/cm<sup>2</sup> G) with ethylene, and then 0.5 g of triethylaluminum and 378.5 mg of the solid catalyst component prepared in Example 5 (B) were injected into the autoclave together with a small amount of n-heptane under an elevated pressure of argon gas. While maintaining the total pressure at 20 bar (20 kg/cm<sup>2</sup>) and the temperature at 60 °C, a homopolymerization of ethylene was carried out for 40 minutes. Then, the unreacted monomer and butane were purged, and a small amount of polymer was sampled to measure  $[\eta]_E$ . Then, 1.05 bar (0.05 kg/cm<sup>2</sup> G) of hydrogen was fed, and the pressure was elevated to 9 bar (8 kg/cm<sup>2</sup> G) with propylene, and then pressure was elevated to 11 bar (10 kg/cm<sup>2</sup> G) with ethylene, after which the temperature was adjusted to 40 °C and the polymerization of step 2 was started.

Then, while feeding an ethylene/propylene gaseous mixture (50%/50% by volume) so as to maintain a total pressure of 11 bar (10 kg/cm<sup>2</sup> G) a copolymerization of ethylene and propylene was carried out in the gas phase for 80 minutes. After the polymerization, the unreacted monomer was purged, and 450 g of a granular thermoplastic elastomer having good powder characteristics were obtained. It contained no fine powder nor coarse particles. Examination of the opened autoclave revealed that no polymer was deposited at all on the inner wall of the autoclave and the stirrer.

The formation of total polymer per 1 g of catalyst (P/cat) was 1,190. Intrinsic viscosities were:  $[\eta]_E = 2.4$ ,  $[\eta]_T = 2.0$  and  $[\eta]_{EP} = 1.9$ . EP content in the total polymer was 90% by weight, and ethylene content in EP was 49% by weight. Adhesive force of the polymer particle thus obtained was 3.1 N/cm<sup>2</sup> (3.2 g/cm<sup>2</sup>).

## Example 8

Using 413.7 mg of the solid catalyst component prepared in Example 6 (A), a block copolymerization of E-EP was carried out under the same conditions as in Example 7 (A). Conditions and results of the polymerization are shown in Table 3 and Table 4, respectively.

## Comparative Example 7

A block copolymerization of E-EP was carried out under the same conditions as in Example 7 (A), except that 144.0 mg of the solid catalyst component prepared in Comparative Example 6 (B) was used and polymerization temperature of EP was lowered to 30 °C. Conditions and results of the polymerization are shown in Table 3 and Table 4, respectively. Since in this experiment the pore volume of solid catalyst component was very small, the particle characteristics of the resulting polymer were very bad, even if the polymerization was carried out at a low temperature.

## Example 9

A solid catalyst component was prepared under the same conditions as in Example 5, except that an ethylene/propylene gaseous mixture (85%/15% by volume) was fed in the step of random copolymerization of ethylene and propylene in Example 5 (C). Using this solid catalyst component, a polymerization was carried out. Conditions and results of the polymerization are shown in Table 3 and Table 4, respectively.

## Example 10

## (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 13.2 g of an acrylonitrile-divinylbenzene copolymer (dVp = 0.68 ml/g) which had been dried under reduced pressure at 80 °C for 60 minutes, 65.5 ml of n-heptane, 0.60 g (1.8 millimoles) of tetrabutoxytitanium and 6.23 g (29.9 millimoles) of tetraethoxysilane were added to

the flask and stirred at 30 °C for 45 minutes.

Then, 16.0 ml of the organomagnesium compound synthesized in Example 1 (A) were dropped from the dropping funnel over a period of 45 minutes, while maintaining the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for 45 minutes and then at 30 °C for 45 minutes, after which the product was washed twice with each 65.5 ml portions of n-heptane and dried under reduced pressure to obtain 16.7 g of a brown colored solid product.

#### (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 5.38 g of the solid product synthesized in (A), 18.0 ml of toluene and 0.82 ml (3.1 millimoles) of diisobutyl phthalate were charged and reacted at 95 °C for one hour.

After the reaction, the solid was separated from the liquid phase and washed twice with each 18.0 ml portions of toluene.

After washing it, 18.0 ml of toluene, 1.2 ml (7.1 millimoles) of n-butyl ether and 21.0 ml (191 millimoles) of titanium tetrachloride were added to the flask and reacted at 95 °C for 3 hours. After the reaction, the solid was separated from the liquid phase at 95 °C and washed at that temperature twice with each 18.0 ml portions of toluene. Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, and the product was washed twice with each 18.0 ml portions of n-heptane, after which it was dried under reduced pressure to obtain 7.61 g of a brown colored solid catalyst component.

It contained 6.2% by weight of titanium atoms 4.0% by weight of magnesium atoms and 1.4% by weight of phthalic ester.

Its mean particle diameter was 80 µm.

#### (C) Polymerization

Using 513.4 mg of the solid catalyst component prepared in (B), a block copolymerization of E-EP was carried out under the same conditions as in Example 5 (C). Conditions and results of the polymerization are shown in Table 3 and Table 4, respectively.

#### Example 11

Using the solid catalyst component prepared in Example 5, a homopolymerization of ethylene was carried out in step 1 and a random copolymerization of ethylene and butene-1 was carried out in step 2.

After drying an autoclave having an inner volume of 5 liters and equipped with a stirrer at 80 °C for one hour, 800 g of butane was fed and the temperature was elevated to 60 °C. Then, hydrogen was fed until its partial pressure reached 4 bar (3 kg/cm<sup>2</sup> G), and the pressure was elevated to 21 bar (20 kg/cm<sup>2</sup> G) by feeding ethylene and then 0.5 g of triethylaluminum, 0.13 g of phenyltrimethoxysilane and 370.5 mg of the solid catalyst component prepared in Example 5 (B) were injected into the autoclave together with a small quantity of n-heptane under a pressure of argon. After carrying out a homopolymerization of ethylene for 45 minutes while maintaining the total pressure at 21 bar (20 kg/cm<sup>2</sup> G) and the temperature at 60 °C, the unreacted monomer and butane were purged and a small amount of polymer was sampled to measure  $[\eta]_E$ . Then 1.074 bar (0.075 kg/cm<sup>2</sup> G) of hydrogen was fed, and an ethylene/butene-1 gaseous mixture (80%/20% by volume) was fed so as to keep a total pressure of 5 bar (4 kg/cm<sup>2</sup> G) and a copolymerization of ethylene and butene-1 was carried out in the gas phase at 75 °C for 420 minutes.

After completion of the polymerization, the unreacted monomer was purged, and 456 g of a thermoplastic elastomer having good particle characteristics were obtained.

Examination of the opened autoclave revealed that no polymer was deposited at all on the inner wall of the autoclave and on the stirrer.

Formation of total polymer per 1 g catalyst (P/cat) was 1,230.

The total polymer contained 85% by weight of the ethylene/butene-1 copolymer formed in step 2. Ethylene content in EB was 80% by weight. Molecular weights of the polymers were as follows:  $[\eta]_E = 1.8$ ,  $[\eta]_{EB} = 3.0$ ,  $[\eta]_T = 2.8$ . The polymer thus obtained had an adhesive force of 43 N/cm<sup>2</sup> (4.4 kg/cm<sup>2</sup>).

## Example 12

## (A) Synthesis of Solid Product

5 After replacing the inner atmosphere of a flask having an inner volume of 1,000 ml and equipped with a stirrer and a dropping funnel with argon gas, 74.0 g of a styrene-divinylbenzene copolymer ( $dV_p = 1.05$  ml/g) which had been dried under reduced pressure at  $80^\circ\text{C}$  for 30 minutes, 370 ml of heptane, 6.69 g (19.7 millimoles) of tetrabutoxytitanium and 70.9 g (340 millimoles) of tetraethoxysilane were charged and stirred at  $30^\circ\text{C}$  for 45 minutes.

10 Then, 180 ml of the organomagnesium compound prepared in Example 1 (A) was dropped from the dropping funnel over a period of 45 minutes, while maintaining the inner temperature of the flask at  $5^\circ\text{C}$ . After dropping it, the content of the flask was stirred at  $5^\circ\text{C}$  for 45 minutes and then at  $30^\circ\text{C}$  for 45 minutes, after which the product was washed twice with each 300 ml portions of hexane and dried under reduced pressure. Thus, 126.3 g of a brown colored solid product was obtained.

15

## (B) Synthesis of Solid Catalyst Component

20 After replacing the inner atmosphere of a flask having an inner volume of 1,000 ml with argon gas, 114.6 g of the solid product synthesized in reduction (A), 382 ml of toluene and 32.1 ml (120 millimoles) of diisobutyl phthalate were charged and reacted at  $95^\circ\text{C}$  for one hour.

After the reaction, the solid was separated from the liquid phase and washed twice with each 300 ml portions of toluene.

25 After washing it, 382 ml of toluene, 25.3 ml (149 millimoles) of butyl ether and 447 ml (4,070 millimoles) of titanium tetrachloride were added to the flask and reacted at  $95^\circ\text{C}$  for 3 hours. After the reaction, the solid product was separated from the liquid phase at  $95^\circ\text{C}$  and washed at that temperature twice with each 300 ml portions of toluene. The above-mentioned treatment using a mixture of butyl ether and titanium tetrachloride was once repeated over a period of one hour, and then the product was washed twice with each 300 ml portions of hexane, after which the product was dried under reduced pressure to obtain 93.9 g of a brown colored solid catalyst component.

30 It contained 0.51% by weight of titanium atoms, 7.2% by weight of magnesium atoms, and 2.5% by weight of phthalic ester.

This solid catalyst component had a mean particle diameter of  $50\ \mu\text{m}$ .

## (C) Polymerization

35

Using an autoclave having an inner volume of 5 liters and equipped with a stirrer, a random copolymerization of ethylene and propylene was carried out.

40 Thus, after charging 50 g of polypropylene powder as a dispersant into the autoclave and evacuating it, its temperature was elevated to  $60^\circ\text{C}$ . Then, 1.6 bar ( $0.61\ \text{kg/cm}^2\ \text{G}$ ) of hydrogen was fed, and an ethylene/propylene gaseous mixture (50%/50% by volume) was fed until the pressure reached 11 bar ( $10\ \text{kg/cm}^2\ \text{G}$ ), after which 0.5 g of triethylaluminum, 0.13 g of phenyltrimethoxysilane and 418.2 mg of the solid catalyst component prepared in (B) were injected into the autoclave together with a small quantity of heptane under a pressure of argon gas. While feeding ethylene/propylene gas so as to maintain a total pressure of 11 bar ( $10\ \text{kg/cm}^2\ \text{G}$ ), a copolymerization of ethylene/propylene was carried out in the gas phase for 50 minutes.

45 After completion of the polymerization, the unreacted monomer was purged, and the polypropylene powder used as dispersant was removed by sieving, and 151 g of a granular elastomer having good powder characteristics which contained neither fine powder nor coarse particles were obtained. No deposition of polymer was found on the inner wall of the autoclave and on the stirrer.

50 Formation (g) of total polymer per 1 gram catalyst (P/cat) was 360. Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

## Comparative Example 8

## 55 (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 1 liter and equipped with a stirrer and a dropping funnel with argon gas, 600 ml of heptane, 7.6 g (22.2 millimoles) of tetrabutox-

ytitanium and 78.1 g (375 millimoles) of tetraethoxysilane were charged, made into a uniform solution, and stirred at room temperature for 30 minutes. Then, 200 ml of the organomagnesium compound synthesized in Example 1 (A) was slowly dropped from the dropping funnel over a period of 3 hours, while keeping the inner temperature of the flask at 5°C. After dropping it, the content of the flask was stirred at room temperature for one hour. The solid was separated from the liquid phase at room temperature and washed thrice with each 600 ml portions of heptane and dried under reduced pressure to obtain 64.5 g of a brown colored solid product.

#### (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 200 ml with argon gas, 13.8 g of the solid product synthesized by reduction (A), 69 ml of toluene and 10.1 ml (37.7 millimoles) of diisobutyl phthalate were charged and reacted at 95°C for one hour.

After the reaction, the solid product was separated from liquid phase and washed twice with each 69 ml portions of toluene.

After washing it, 69 ml of toluene, 5.0 ml (30 millimoles) of butyl ether and 88.5 ml (805 millimoles) of titanium tetrachloride were charged into the flask and reacted at 95°C for 3 hours. After the reaction, the solid product was separated from the liquid phase at 95°C and washed at that temperature twice with each 69 ml portions of toluene. The above-mentioned treatment using a mixture of butyl ether and titanium tetrachloride was once repeated over a period of one hour, and then the product was washed twice with each 69 ml portions of n-heptane, after which it was dried under reduced pressure to obtain 10.4 g of a brown colored solid catalyst component.

It contained 1.8% by weight of titanium atoms 21% by weight of magnesium atoms and 6.5% by weight of phthalic ester.

#### (C) Polymerization

Using the solid catalyst component obtained above, a copolymerization of ethylene and propylene was carried out in the same manner as in Example 12 (C). Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

Since in this experiment the solid catalyst component was not impregnated in a porous polymer carrier, the particle characteristics were very bad. Thus, examination of the opened autoclave revealed that the polymer particles adhered to the polypropylene powder dispersant and formed masses.

#### Comparative Example 9

##### (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 300 ml and equipped with a stirrer and a dropping funnel with argon gas, 10.0 g of silica gel (dVp = 0.69 ml/g) which had been calcined at 700°C for 8 hours in an atmosphere of nitrogen, 50.0 ml of n-heptane, 1.31 g (3.86 millimoles) of tetrabutoxytitanium and 13.8 g (66.1 millimoles) of tetraethoxysilane were charged and stirred at 30°C for 45 minutes.

Then, 35.5 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of 45 minutes while keeping the inner temperature of the flask at 5°C. After dropping it, the content of the flask was stirred at 5°C for 45 minutes and then at 30°C for 45 minutes, and the produce was washed twice with each 50 ml portions of heptane and dried under reduced pressure to obtain 21.0 g of a brown colored solid product.

##### (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 200 ml with argon gas, 9.34 g of the solid product formed by reduction (A), 31.1 ml of toluene and 3.53 ml (13.2 millimoles) of diisobutyl phthalate were charged and reacted at 95°C for one hour.

After the reaction, the solid matter was separated from the liquid phase and washed twice with each 31 ml portions of toluene. Then, 31.1 ml of toluene, 2.06 ml (12.2 millimoles) of butyl ether and 36.4 ml (331 millimoles) of titanium tetrachloride were added to the flask and reacted at 95°C for 3 hours. After the reaction, the solid product was separated from liquid phase at 95°C and washed at that temperature twice

with each 31 ml portions of toluene. Then, the above-mentioned treatment using a mixture of butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 31 ml portions of heptane and dried under reduced pressure. Thus, 8.23 g of a brown colored solid catalyst component was obtained.

5 The solid catalyst component contained 2.4% by weight of titanium atoms, 5.0% by weight of magnesium atoms and 2.5% by weight of phthalic ester. Its mean particle diameter was 60  $\mu\text{m}$ .

### (C) Polymerization

10 Using the solid catalyst component obtained above, a copolymerization of ethylene and propylene was carried out in the same manner as in Example 12 (C).

Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

Since in this experiment the solid catalyst component was impregnated in silica gel instead of an organic porous polymer carrier, the particle characteristics of the product were very bad. Thus, examination  
15 of the opened autoclave revealed that polymer particles adhered to the polypropylene powder dispersant to form masses.

### Comparative Example 10

#### 20 (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and was equipped with a stirrer and a dropping funnel with argon gas, it was charged with 5.0 g of a styrene-divinylbenzene copolymer ( $dV_p = 0.08 \text{ ml/g}$ , pore volume including the pores having a pore radius smaller than  $100 \cdot 10^{-10} \text{ m}$  (100 Å) and greater than  $5,000 \cdot 10^{-10} \text{ m}$  (5,000 Å) was 0.93 ml/g) which had been vacuum-dried at  
25  $80^\circ \text{C}$  for one hour, together with 25.0 ml of heptane, 0.28 g (0.67 millimoles) of tetrabutoxytitanium and 2.42 g (11.6 millimoles) of tetraethoxysilane and stirred at  $30^\circ \text{C}$  for 45 minutes.

Then, 6.1 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of one hour while keeping the inner temperature of the flask at  $5^\circ \text{C}$ . After  
30 dropping it, the content of the flask was stirred at  $5^\circ \text{C}$  for 45 minutes and then at  $30^\circ \text{C}$  for 45 minutes, after which the product was washed thrice with each 30 ml portions of heptane and dried under reduced pressure. Thus, 5.7 g of a brown colored solid product was obtained.

#### (B) Synthesis of Solid Catalyst Component

35 After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 5.6 g of the solid product synthesized by reduction (A), 18.7 ml of toluene and 0.50 ml (1.9 millimoles) of diisobutyl phthalate were charged and reacted at  $95^\circ \text{C}$  for one hour.

After the reaction, the solid product was separated from the liquid phase and washed twice with each  
40 18.7 ml portions of toluene.

After washing it, 18.7 ml of toluene, 1.24 ml (7.3 millimoles) of butyl ether and 21.9 ml (199 millimoles) of titanium tetrachloride were charged into the flask and reacted at  $95^\circ \text{C}$  for 3 hours. After the reaction, the solid product was separated from the liquid phase at  $95^\circ \text{C}$  and washed at that temperature twice with each  
45 18.7 ml portions of toluene. The above-mentioned treatment using a mixture of butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 18.7 ml portions of heptane and dried under reduced pressure. Thus, 4.7 g of a red-brown colored solid product were obtained.

Analyses revealed that the solid catalyst component thus obtained contained no magnesium atoms nor phthalic ester, though it contained a trace quantity of titanium atoms.

50

### (C) Polymerization

Using the solid catalyst component synthesized in (B), a copolymerization of ethylene and propylene was carried out under the same conditions as in Example 12 (C). However, no polymer could be obtained.

55 Since the organic porous polymer carrier used in this example had a much smaller  $dV_p$  in the pore radius range of 100 to  $5,000 \cdot 10^{-10} \text{ m}$  (100 to 5,000 Å) than the carrier of Example 1, it could not hold the catalyst component having catalyst activity in its porous polymer, so that the catalyst of this example could not function as an effective catalyst for ethylene/propylene copolymerization.

## Examples 13 and 14

Using the solid catalyst component prepared in Example 12 (B), a random copolymerization of ethylene and propylene was carried out in the same manner as in Example 12 (C), except that the amount of solid catalyst, temperature of polymerization, partial pressure of hydrogen, composition of ethylene/propylene gas mixture and polymerization time were altered as shown in Table 5. Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

## Example 15

## (A) Synthesis of solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 2.74 g of the solid product synthesized by reduction of Example 12 (A), 9.1 ml of toluene, 0.60 ml (3.5 millimoles) of n-butyl ether and 10.6 ml (96.4 millimoles) of titanium tetrachloride were charged and reacted at 95 °C for 3 hours. After the reaction, the solid product was separated from liquid phase at 95 °C and washed at that temperature twice with each 10 ml portions of toluene. The above-mentioned treatment using a mixture of butyl ether and titanium tetrachloride was once repeated, after which the product was washed twice with each 10 ml portions of heptane and dried under reduced pressure. Thus, 2.47 g of a brown colored solid catalyst component were obtained. It contained 2.0% by weight of titanium atoms and 6.9% by weight of magnesium atoms. Its mean particle diameter was 50  $\mu\text{m}$ .

## (B) Polymerization

Using 378.5 mg of the solid catalyst component prepared in (A), a random copolymerization of ethylene and propylene was carried out in the same manner as in Example 12 (C). Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

## Example 16

Using the solid catalyst component prepared in Example 15 (A), a random copolymerization of ethylene and propylene was carried out in the same manner as in Example 12 (C), except that the amount of solid catalyst, partial pressure of hydrogen and time of polymerization were altered as shown in Table 5 and no electron donor was used. Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

## Example 17

Using the solid catalyst component prepared in Example 12 (B), a random copolymerization of ethylene, propylene and 1,9-decadiene was carried out in a 5 liter autoclave equipped with a stirrer.

Fifty grams of polypropylene powder was charged into an autoclave as a dispersant and the pressure in the autoclave was reduced, and then its temperature was elevated to 60 °C. Then, 1.4 bar (0.41 kg/cm<sup>2</sup> G) of hydrogen was fed, and pressure was elevated to 11.5 bar (10 kg/cm<sup>2</sup> G) with a ethylene/propylene gaseous mixture (50%/50% by volume), after which 0.5 g of triethylaluminum and 0.13 g of phenyltrimethoxysilane were injected into the autoclave together with a small quantity of heptane under pressure of argon. Then, 15 ml of 1,9-decadiene was injected into the autoclave under a pressure of argon, and then 331.0 mg of the solid catalyst component prepared in Example 12 (B) were injected into the autoclave together with a small amount of heptane under a pressure of argon. While feeding the ethylene/propylene gaseous mixture to maintain a total pressure of 11 bar (10 kg/cm<sup>2</sup> G), a random copolymerization of ethylene, propylene and 1,9-decadiene was carried out for 60 minutes.

After completion of the polymerization, the unreacted monomers were purged, and 140 g of a granular elastomer having good powder characteristics which contained no fine powder nor coarse particles were obtained. No deposition of polymer was observed at all on the inner wall of the autoclave and the stirrer.

Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

## Example 18

Using the solid catalyst component prepared in Example 12 (B), a random copolymerization of ethylene and butene-1 was carried out in a 5 liter autoclave equipped with a stirrer.

5 After charging 50 g of polypropylene powder as a dispersant and reducing the pressure of autoclave, its temperature was elevated to 60 °C. Then, 1.33 bar (0.34 kg/cm<sup>2</sup> G) of hydrogen was fed, and the pressure was elevated to 6 bar (5 kg/cm<sup>2</sup> G) with an ethylene/butene-1 gaseous mixture (80%/20% by volume), and then 0.5 g of triethylaluminum, 0.13 g of phenyltrimethoxysilane and 408.3 mg of the solid catalyst component prepared in Example 12 (B) were injected into the autoclave together with a small amount of  
10 heptane under a pressure of argon. While feeding the ethylene/butene-1 gaseous mixture so as to maintain a total pressure of 6 bar (5 kg/cm<sup>2</sup> G), a copolymerization of ethylene/butene-1 was carried out in the gas phase for 60 minutes.

After completion of the polymerization, the unreacted monomers were purged, and 93 g of a granular elastomer having good particle characteristics which contained neither fine powders nor coarse particles  
15 were obtained. No deposition of polymer was observed on the inner wall of the autoclave and the stirrer. Conditions and results of the polymerization are shown in Table 5 and Table 6, respectively.

## Example 19

20 Using the solid catalyst component prepared in Example 12 (B), a random copolymerization of ethylene and butene-1 was carried out in a fluidized bed type gas phase polymerization reactor having a volume of 26 liters.

After heating the reactor to 70 °C, 300 g of a polypropylene powder previously dried under reduced pressure were introduced into the reactor as a dispersant, and then 4.26 g of triethylaluminum, 1.11 g of  
25 phenyltrimethoxysilane and 1.20 g of the solid catalyst component prepared in Example 12 (B) were injected into the reactor together with a small quantity of hexane under an elevated pressure. A gaseous mixture of ethylene, butene-1 and hydrogen having a molar ratio of ethylene/butene-1/hydrogen of 53/26.5/20.5 was circulated in the reactor at a flow rate of 0.3 m/second under a pressure of 8 to 8.5 bar (7 to 7.5 kg/cm<sup>2</sup> G). When the molar ratio of ethylene/butene-1/hydrogen deviated from the predetermined  
30 value, some of the gases was additionally fed to adjust the molar ratio. Under this condition, a gas phase copolymerization of ethylene and butene-1 was carried out for 7 hours on the fluidized bed, while maintaining the ratio of polymer height in the reactor to the diameter of reactor (L/d) in the range of 2 to 4. After completion of the polymerization, an amount of polymer, corresponding to the formation of polymer, was withdrawn from the reactor, and the polymer remaining in the reactor was used as the dispersant for  
35 the subsequent run of polymerization. When the polymerization had been repeated six times by the above-mentioned procedure, the percentage of the initially used polypropylene powder in the polymer had become negligibly small.

The polymer thus obtained had good powder characteristics and contained neither fine powders nor coarse particles. It contained 82.8% by weight of ethylene, and had an intrinsic viscosity [ $\eta$ ] of 1.4 and an  
40 adhesive force of 45 N/cm<sup>2</sup> (4.6 g/cm<sup>2</sup>). Formation of total polymer per 1 gram solid catalyst throughout the six runs of polymerization (P/cat) was 540.

## Comparative Example 11

## 45 (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 100 ml and equipped with a stirrer and a dropping funnel with argon gas, 6.00 g of a styrene-divinylbenzene copolymer (dVp = 0.75 ml/g, mean particle diameter = 1,300  $\mu$ m) which had been dried under reduced pressure at 80 °C for 30  
50 minutes, 30.0 ml of heptane, 0.27 g (0.79 millimoles) of tetrabutoxytitanium and 2.88 g (13.8 millimoles) of tetraethoxysilane were charged and stirred at 30 °C for 45 minutes.

Then, 7.3 ml of the organomagnesium compound synthesized in Example 1 (A) were dropped from the dropping funnel over a period of 45 minutes, while keeping the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for 45 minutes and then at 30 °C for 45 minutes,  
55 after which the product was washed twice with each 30.0 ml portions of heptane and dried under reduced pressure to obtain 7.45 g of a brown colored solid product.

## (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 6.71 g of the solid product prepared by reduction (A), 22.4 ml of toluene and 0.92 ml (3.44 millimoles) of diisobutyl phthalate were charged and reacted at 95 °C for one hour.

After the reaction, the solid product was separated from liquid phase and washed twice with each 22.4 ml portions of toluene. Then, 22.4 ml of toluene, 1.48 ml (8.74 millimoles) of butyl ether and 26.2 ml (238 millimoles) of titanium tetrachloride were charged into the flask and reacted at 95 °C for 3 hours. After the reaction, the solid product was separated from liquid phase at 95 °C and washed at that temperature twice with each 22.4 ml portions of toluene. Then, the above-mentioned treatment using a mixture of butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 22.4 ml portions of heptane and dried under reduced pressure to obtain 5.73 g of a brown colored solid catalyst component.

The solid catalyst component thus obtained contained 0.14% by weight of titanium atoms, 2.5% by weight of magnesium atoms and 0.9% by weight of phthalic ester.

## (C) Polymerization

Using the solid catalyst component obtained above, a copolymerization of ethylene and butene-1 was carried out in the same manner as in Example 19. However, since the catalyst was not dispersed sufficiently, the state of flow became instable with progress of polymerization, and the fluidized bed gas phase copolymerization was impossible to continue. The resulting polymer contained a large amount of massive polymer and hollow polymer.

Since the organic porous polymer carrier used in the solid catalyst component of this example had much greater mean particle diameter than that of Example 19, no stable flow state could be realized in the fluidized bed gas phase polymerization of ethylene and butene-1.

## Example 20

## (A) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 3,000 ml and equipped with a stirrer and a dropping funnel with argon gas, 299 g of a styrene-divinylbenzene copolymer (dVp = 0.68 ml/g) which had been dried under reduced pressure at 110 °C for 360 minutes, 1,500 ml of heptane, 10.1 g (29.9 millimoles) of tetrabutoxytitanium and 107.0 g (514 millimoles) of tetraethoxysilane were charged and stirred at 30 °C for 45 minutes.

Then, 272 ml of the organomagnesium compound synthesized in Example 1 (A) were dropped from the dropping funnel over a period of 70 minutes while keeping the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for 45 minutes and then at 30 °C for 45 minutes, after which the product was washed twice with each 1,500 ml portions of heptane and then twice with each 1,500 ml portions of toluene.

Then, 1,240 ml of toluene and 99.2 ml (371 millimoles) of diisobutyl phthalate were added and reacted at 95 °C for 30 minutes.

After the reaction, the solid product was separated from the liquid phase and washed twice with each 1,240 ml portions of toluene.

After washing it, 1,100 ml of toluene, 73.0 ml (431 millimoles) of n-butyl ether and 1,300 ml (11.83 moles) of titanium tetrachloride were added to the flask and reacted at 95 °C for 3 hours. After the reaction, the solid product was separated from liquid phase at 95 °C and washed at that temperature twice with each 1,200 ml portions of toluene. Then, the above-mentioned treatment using a mixture of butyl ether and titanium tetrachloride was once repeated over a period of one hour, and the product was washed twice with each 1,200 ml portions of heptane, after which it was dried under reduced pressure to obtain 345 g of a brown colored solid catalyst component.

The solid catalyst component thus obtained contained 0.20% by weight of titanium atoms, 2.5% by weight of magnesium atoms and 1.3% by weight of phthalic ester.

This solid catalyst component had a mean particle diameter of 40 μm.

## (B) Synthesis of Preliminary Polymerization Catalyst

After thoroughly replacing the inner atmosphere of a reactor having an inner volume of 2 liters and equipped with a stirrer with nitrogen gas, 68 g of the solid catalyst component obtained in (A), 1,350 ml of hexane, 1.33 g of triethylaluminum and 0.35 g of phenyltrimethoxysilane were charged, and stirring was started. Then, the temperature was adjusted to 18°C to 20°C, and 340 g of propylene were fed and polymerized over a period of 3 hours. The reaction mixture was filtered and the solid product was dried at 40°C under reduced pressure to obtain 340 g of a preliminary polymerization catalyst.

By repeating the above-mentioned procedure twice additionally, 1,000 g of a preliminary polymerization catalyst were obtained

## (C) Polymerization

Using the preliminary polymerization catalyst obtained above, a random copolymerization of ethylene and butene-1 was carried out in a fluidized bed type gas phase polymerization reactor having an inner volume of 1.5 m<sup>3</sup>.

First, 70 kg of propylene polymer particle was charged into the reactor as a dispersant for catalyst, and thereafter a gaseous mixture composed of 55.2% by mole of ethylene, 42.0% by mole of propylene and 2.8% by mole of hydrogen was circulated by means of a gas circulator at a rate of 140 m<sup>3</sup>/hour (flow rate 0.2 m/second) under a pressure of 11 bar (10 kg/cm<sup>2</sup> G) at a temperature of 70°C.

Then, the preliminary polymerization catalyst, triethylaluminum and phenyltrimethoxysilane were continuously fed into the reactor at a rate of 9.6 g/hour, 3.9 g/hour and 0.77 g/hour, respectively, and copolymerization was carried out. The resulting excessive polymer was successively discharged out of the reactor, and the polymerization was continued for 61 hours. Thus, the polymerization could be carried out stably without any trouble.

The quantity of polymerization was 9.8 kg/hour, and quantity of polymerization per unit weight of solid catalyst was 5,100 g/g. The polymer thus obtained had good powder characteristics and contained neither fine powder nor coarse particles. It contained 82.4% by weight of ethylene and had an intrinsic viscosity [ $\eta$ ] of 2.9 and an adhesive force of 2.2 g/cm<sup>2</sup>.

## Example 21

## (A) Polymerization of Propylene

After replacing the inner atmosphere of a stainless steel autoclave having an inner volume of 130 ml and equipped with a magnetic stirrer with argon gas, 0.57 millimole of triethylaluminum, 0.057 millimole of phenyltriethoxysilane, 45.0 mg of the solid catalyst component obtained in Example 1 (C) and 80 ml of liquefied propylene were charged into the autoclave.

While stirring the content of the autoclave, it was kept at 60°C for one hour. After purging the excessive propylene, the resulting polypropylene was air-dried overnight. Thus, 11.7 g of polypropylene were obtained.

Accordingly, the yield (g) of polypropylene per 1 g titanium present in the solid catalyst component (PP/Ti) was 52,000.

When the polypropylene powder thus obtained was extracted with boiling n-heptane for 6 hours, the quantity of unextractable residue [expressed by percentage, hereinafter referred to as "IY (%)"] was 93.9%. Bulk density [hereinafter referred to as BD (g/ml)] of the propylene powder was 0.43 g/ml.

## (B) Measurement of Particle Size Distribution of Polypropylene Powder

The polypropylene powder obtained in (A) was fractionated by means of JIS Standard Wire Screen having mesh sizes of 0.125 to 3.36 mm. Then, the polymer remaining on each sieve was weighed, and its ratio to the total polymer weight was calculated. The results were cumulated from the side of smaller particle size. Table 7 and Figure 2 illustrate the cumulative fractions (% by weight) by screening. Bulk density (BD) is also shown in Table 7.

## Comparative Example 12

## (A) Synthesis of Solid Product

5 After replacing the inner atmosphere of a flask having an inner volume of 1 liter and equipped with a stirrer and a dropping funnel with argon gas, 600 ml of n-heptane, 7.6 g (22.2 millimoles) of tetrabutoxytitanium and 78.1 g (375 millimoles) of tetraethoxysilane were charged, formed into a uniform solution, and stirred at room temperature for 30 minutes. Then, 200 ml of the organomagnesium compound synthesized in Example 1 (A) were slowly dropped from the dropping funnel over a period of 3 hours, while keeping the  
 10 inner temperature of the flask at 5°C. After dropping it, the content of the flask was stirred at room temperature for an additional one hour, and then the solid product was separated from liquid phase at room temperature, washed thrice with each 600 ml portions of n-heptane and dried under reduced pressure to obtain 64.5 g of a brown colored solid product.

## 15 (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 200 ml with argon gas, 17.10 g of the solid product synthesized in reduction (A), 85.5 ml of monochlorobenzene and 3.76 ml (14.0 millimoles) of diisobutyl phthalate were added and reacted at 80°C for one hour.

20 After the reaction, the solid product was separated from the liquid phase and washed twice with each 90 ml portions of n-heptane.

After washing it, 85.5 ml of monochlorobenzene, 5.64 ml (33.3 millimoles) of n-butyl ether and 100.9 ml (918 millimoles) of titanium tetrachloride were added to the flask and reacted at 80°C for 3 hours. After the reaction, the solid product was separated from the liquid phase at 80°C and washed at that temperature  
 25 twice with each 90 ml portions of monochlorobenzene.

The above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 90 ml portions of n-heptane and dried under reduced pressure. Thus, 14.4 g of a brown colored solid catalyst was obtained.

30 The solid catalyst component thus obtained contained 2.7% by weight of titanium atoms, 21% by weight of magnesium atoms and 9.7% by weight of phthalic ester.

## (C) Polymerization

35 Using the solid catalyst component obtained above, a polymerization of propylene was carried out in the same manner as in Example 21 (A). The results were as follows: PP/Ti = 153,000, IY = 96.4%, BD = 0.30 g/ml.

The particle size distribution of the polypropylene powder obtained herein was measured in the same manner as in Example 21 (B) to obtain the results shown in Table 7 and Figure 2.

Since in this experiment the solid catalyst component was not supported on porous polymer beads, bulk density of the polymer was much lower than that in Example 21. The polymer obtained in this example contained a very large amount of fine powder having a size smaller than 500 µm.

## Example 22

## 45 (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 9.9 g of a styrene-divinylbenzene copolymer (dVp = 1.05 ml/g) which had been dried under reduced pressure at 80°C for one hour, 49.5 ml of n-heptane, 0.90 g (2.6 millimoles) of tetrabutoxytitanium and 9.49 g (45.5 millimoles) of tetraethoxysilane were charged and stirred  
 50 at 30°C for 45 minutes.

Then, 24.0 ml of the organomagnesium compound synthesized in Example 1 (A) were dropped from the dropping funnel over a period of one hour while keeping the inner temperature of the flask at 5°C. After dropping it, the content of the flask was stirred at 5°C for 45 minutes and then at 30°C for 45 minutes,  
 55 after which the product was washed thrice with each 50 ml portions of n-heptane and dried under reduced pressure to obtain 15.9 g of a brown colored solid product.

The solid product contained 0.54% by weight of titanium atom and 4.2% by weight of magnesium atoms.

## (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 6.8 g of the solid product synthesized in (A), 22.7 ml of toluene and 1.8 ml (6.7 millimoles) of diisobutyl phthalate were added and reacted at 95 °C for one hour.

After the reaction, the solid product was separated from the liquid phase and washed twice with each 23 ml portions of toluene.

After washing it, 22.7 ml of toluene, 1.5 ml (8.9 millimoles) of n-butyl ether and 26.5 ml (241 millimoles) of titanium tetrachloride were added to the flask and reacted at 95 °C for 3 hours. After the reaction, the solid product was separated from the liquid phase at 95 °C and washed at that temperature twice with each 23 ml portions of toluene. Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 23 ml portions of n-heptane and dried under reduced pressure to obtain 5.5 g of a brown colored solid catalyst component.

It contained 0.46% by weight of titanium atoms, 5.4% by weight of magnesium atoms and 1.5% by weight of phthalic ester.

## (C) Polymerization

Using the solid catalyst component prepared in (B), a polymerization of propylene was carried out under the same conditions as in Example 21 (A). The results were as follows: PP/Ti = 233,000, IY = 95.7%, BD = 0.35 g/ml.

Particle size distribution of the polypropylene powder thus obtained was determined in the same manner as in Example 21 (B) to obtain the results shown in Table 7 and Figure 2.

## Example 23

## (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 7.0 g of a styrene-divinylbenzene copolymer (dVp = 0.91 ml/g) which had been dried under reduced pressure at 80 °C for one hour and 28 ml of n-butyl ether were charged and stirred. With stirring, 20.0 ml of the organomagnesium compound synthesized in Example 1 (A) were dropped from the dropping funnel over a period of 10 minutes while keeping the inner temperature of the flask at 80 °C, and thereafter the content of the flask was reacted at that temperature for one hour. After washing the product twice with each 28 ml portions of n-butyl ether and twice with each 28 ml portions of n-heptane, it was dried under reduced pressure to obtain 7.0 g of an organomagnesium-treated product.

Then, after replacing the inner atmosphere of a flask having an inner volume of 100 ml and equipped with a stirrer and a dropping funnel with argon gas, 7.0 g of the organomagnesium-treated product synthesized above, 35 ml of n-heptane, 0.62 g (1.8 millimoles) of tetrabutoxytitanium and 6.31 g (30.3 millimoles) of tetraethoxysilane were charged and stirred at 30 °C for 30 minutes.

Then, 16.0 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of one hour, while keeping the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for one hour and then at room temperature for one hour, after which the product was washed thrice with each 35 ml portions of n-heptane and dried under reduced pressure to obtain 11.6 g of a brown colored solid product.

The solid product thus obtained contained 0.46% by weight of titanium atoms and 5.1% by weight of magnesium atoms.

## (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 4.22 g of the solid product synthesized in (A), 14.0 ml of toluene and 0.94 ml (3.5 millimoles) of diisobutyl phthalate were charged and reacted at 95 °C for one hour.

After the reaction, the solid product was separated from liquid phase and washed twice with each 20 ml portions of toluene.

After washing it, 14.0 ml of toluene, 0.93 ml (5.1 millimoles) of n-butyl ether and 16.4 ml (149 millimoles) of titanium tetrachloride were charged into the flask and reacted at 95 °C for 3 hours. After the

reaction, the solid product was separated from liquid phase at 95°C and washed at that temperature twice with each 20 ml portions of toluene. Then, the above-mentioned treatment using a mixture of *n*-butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 20 ml portions of *n*-heptane and dried under reduced pressure to obtain 3.65 g of a brown

5 colored solid catalyst component.

The solid catalyst component thus obtained contained 0.41% by weight of titanium atoms, 5.2% by weight of magnesium atoms and 1.0% by weight of phthalic ester.

### (C) Polymerization

10

Using the solid catalyst component synthesized above, a polymerization of propylene was carried out under the same conditions as in Example 21 (A). The results were as follows: PP/TI = 124,000, IY = 93.9%, BD = 0.45 g/ml.

The particle size distribution of the polypropylene obtained herein was determined in the same manner as in Example 21 (B) to obtain the results shown in Table 7.

15

### Comparative Example 13

#### (A) Synthesis of Solid Product

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After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 5.0 g of a styrene-divinylbenzene copolymer (dVp = 0.08 ml/g; its pore volume including the pores having a pore radius smaller than  $100 \cdot 10^{-10}$  m (100 Å) and greater than  $5,000 \cdot 10^{-10}$  m (5,000 Å) was 0.93 ml/g) which had been dried under reduced pressure at 80°C for one hour, 25.0 ml of *n*-heptane, 0.23 g (0.67 millimoles) of tetrabutoxytitanium and 2.42 g (11.6 millimoles) of tetraethoxysilane were charged and stirred at 30°C for 45 minutes.

25

Then, 6.1 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of one hour while keeping the inner temperature of the flask at 5°C. After dropping it, the content of the flask was stirred at 5°C for 45 minutes and then at 30°C for 45 minutes, after which the product was washed thrice with each 30 ml portions of *n*-heptane and dried under reduced pressure to obtain 5.7 g of a solid product.

30

The solid product contained 0.3% by weight of titanium atoms and 2.5% by weight of magnesium atoms.

#### 35 (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 5.6 g of the solid product obtained in (A), 18.7 ml of toluene and 0.50 ml (1.9 millimoles) of diisobutyl phthalate were charged and reacted at 95°C for one hour.

After the reaction, the solid product was separated from the liquid phase and washed twice with each 18.7 ml portions of toluene.

After washing it, 18.7 ml of toluene, 1.24 ml (7.3 millimoles) of *n*-butyl ether and 21.9 ml (199 millimoles) of titanium tetrachloride were added to the flask and reacted at 95°C for 3 hours. After the reaction, the solid product was separated from the liquid phase at 95°C and washed at that temperature twice with each 18.7 ml portions of toluene. Then, the above-mentioned treatment using a mixture of *n*-butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 18.7 ml portions of *n*-heptane and dried under reduced pressure to obtain 4.7 g of a red-brown colored solid catalyst component.

45

Analyses of the solid catalyst component thus obtained revealed that no magnesium atoms and phthalic ester were detected, though a trace quantity of titanium atoms were detected.

50

### (C) Polymerization

Using the solid catalyst component synthesized above, a polymerization of propylene was carried out under the same conditions as in Example 21 (A), however, no polymer was obtained.

55

Since the porous polymer beads used in this experiment had a smaller pore volume (dVp) in the pore radius range of 100 to  $5,000 \cdot 10^{-10}$  m (100 to 5,000 Å) as compared with the porous polymer beads used in Examples 21, 22 and 23, the catalyst component having polymerization activity could not be held in the

porous polymer, so that it could not function as an effective catalyst for polymerization of propylene.

#### Example 24

##### 6 (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 300 ml and equipped with a stirrer and a dropping funnel with argon gas, 20.7 g of polyvinyl chloride (dVp = 0.27 ml/g) which had been dried under reduced pressure at 80 °C for one hour and 68 ml of n-butyl ether were charged. While stirring  
 10 the content of the flask, 68 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of 30 minutes during which the inner temperature of the flask was kept at 30 °C, and reacted at that temperature for one hour.

Then, the product was washed twice with each 42 ml portions of n-butyl ether and twice with each 85 ml portions of n-heptane and dried under reduced pressure to obtain 20.3 g of an organomagnesium-treated  
 15 product.

Then, after replacing the inner atmosphere of a flask having an inner volume of 100 ml and equipped with a stirrer and a dropping funnel with argon gas, 9.3 g of the organomagnesium-treated product prepared above, 46 ml of n-heptane, 0.32 g (0.94 millimoles) of tetrabutoxytitanium and 3.3 g (16 millimoles) of tetraethoxysilane were charged and stirred at 30 °C for 45 minutes.

20 Then, 8.4 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of one hour while keeping the inner temperature of the flask at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for one hour and then at room temperature for one hour, after which the product was washed thrice with each 46 ml portions of n-heptane and dried under reduced pressure to obtain 10.5 g of a brown colored solid product.

25 The solid product thus obtained contained 0.2% by weight of titanium atoms and 2.4% by weight of magnesium atoms.

##### (B) Synthesis of Solid Catalyst Component

30 After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 5.1 g of the solid product obtained in (A), 17.0 ml of toluene and 0.43 ml (1.6 millimoles) of diisobutyl phthalate were charged and reacted at 95 °C for one hour.

After the reaction, the solid product was separated from liquid phase and washed twice with each 17 ml portions of toluene.

35 After washing it, 17.0 ml of toluene, 1.12 ml (6.6 millimoles) of n-butyl ether and 20.0 ml (182 millimoles) of titanium tetrachloride were added to the flask and reacted at 95 °C for 3 hours. After the reaction, the solid product was separated from liquid phase at 95 °C and washed at that temperature twice with each 17 ml portions of toluene. Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed  
 40 twice with each 17 ml portions of n-heptane and dried under reduced pressure to obtain 3.8 g of a brown colored solid catalyst component.

The solid catalyst component thus obtained contained 0.1% by weight of titanium atoms, 1.5% by weight of magnesium atoms and 0.4% by weight of phthalic ester.

##### 45 (C) Polymerization

Using the solid catalyst component synthesized in (B), a polymerization of propylene was carried out under the same conditions as in Example 21 (D). The results were as follows: PP/Ti = 100,000, IY = 95.5%, BD = 0.34 g/ml. The particle size distribution of the polypropylene powder thus obtained was  
 50 determined in the same manner as in Example 21 (B) to obtain the results shown in Table 7.

#### Example 25

##### (A) Polymerization in Liquefied Propylene

55 After replacing the inner atmosphere of a 3 liter stainless steel autoclave equipped with a stirrer with argon gas, 2.6 millimoles of triethylaluminum, 0.39 millimole of phenyltrimethoxysilane and 31.9 mg of the solid catalyst component synthesized in Example 22 were charged, and then hydrogen was fed until its

partial pressure reached 0.12 bar (0.12 kg/cm<sup>2</sup>). Then, 780 g of liquefied propylene was charged, the temperature of the autoclave was elevated to 80 °C, and polymerization was carried out at 80 °C for 2 hours.

After the polymerization, the unreacted monomers were purged. The resulting polymer was dried under reduced pressure at 60 °C for 2 hours. Thus, 118 g of a polypropylene powder were obtained.

Accordingly, PP/Ti was equal to 804,000. The proportion of cold xylene-soluble atactic component in the total yield of polymer [hereinafter referred to as CXS (%)] was equal to 2.0% by weight. Further, BD was 0.36 g/ml.

#### 10 (B) Preparation of Biaxially Stretched Film

Using a portable test press, the polymer obtained in (A) was formed into a sheet having a thickness of 500 µm by pre-heating the polymer at 230 °C for 5 minutes, pressing it up to a pressure of 81 bar (80 kg/cm<sup>2</sup> G) in 3 minutes, and thereafter keeping the pressure of 81 bar (80 kg/cm<sup>2</sup> G) for one minute. The sheet thus obtained was cut into a size of 90 x 90 mm, and subjected to biaxial stretching under the following conditions. Using a portable biaxial stretching machine, the sheet was pre-heated at 155 °C for 3.5 minutes and then stretched to 5 times its initial length, in both longitudinal and lateral directions, at a speed of 5 m/minute. Thus, a biaxially stretched film was obtained.

Microscopic examination of the film thus obtained did not reveal existence of fish eyes.

#### 20 Comparative Example 14

##### (A) Synthesis of Solid Product

After replacing the inner atmosphere of a flask having an inner volume of 200 ml and equipped with a stirrer and a dropping funnel with argon gas, 15.0 g of silica gel (dVp = 0.83 ml/g) which had been dried under reduced pressure at 100 °C and 45.5 ml of n-butyl ether were charged. While stirring the content of the flask, 42 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of 10 minutes during which the inner temperature of the flask was kept at 30 °C, and then reacted at that temperature for 2 hours.

After washing the product twice with each 20 ml portions of n-butyl ether and twice with each 40 ml portions of n-heptane, it was dried under reduced pressure to obtain 14.8 g of an organomagnesium-treated product.

Then, after replacing the inner atmosphere of a flask having an inner volume of 300 ml and equipped with a stirrer and a dropping funnel with argon gas, 13.8 g of the organomagnesium-treated product, 69 ml of n-heptane, 0.77 g (2.3 millimoles) of tetrabutoxytitanium and 8.0 g (38.6 millimoles) of tetraethoxysilane were charged and stirred at 30 °C for 30 minutes.

Then, 22.6 ml of the organomagnesium compound synthesized in Example 1 (A) was dropped from the dropping funnel over a period of 2 hours during which the inner temperature of the flask was kept at 5 °C. After dropping it, the content of the flask was stirred at 5 °C for one hour and then at room temperature for one hour, after which the product was washed thrice with each 60 ml portions of n-heptane and dried under reduced pressure to obtain 21.1 g of a brown colored solid product.

The solid product thus obtained contained 0.53% by weight of titanium atoms and 5.9% by weight of magnesium atoms.

#### 45 (B) Synthesis of Solid Catalyst Component

After replacing the inner atmosphere of a flask having an inner volume of 100 ml with argon gas, 5.6 g of the solid product synthesized in (A), 18.8 ml of toluene and 0.74 ml (2.8 millimoles) of diisobutyl phthalate were added to the flask and reacted at 95 °C for one hour.

After the reaction, the solid product was separated from the liquid phase and washed twice with each 18.8 ml portions of toluene.

After washing it, 18.8 ml of toluene, 0.65 ml (3.8 millimoles) of n-butyl ether and 11.6 ml (106 millimoles) of titanium tetrachloride were added to the flask and reacted at 95 °C for 3 hours. After the reaction, the solid product was separated from liquid phase at 95 °C and washed at that temperature twice with each 18.8 ml portions of toluene. Then, the above-mentioned treatment using a mixture of n-butyl ether and titanium tetrachloride was once repeated over a period of one hour, after which the product was washed twice with each 18.8 ml portions of n-heptane and dried under reduced pressure to obtain 4.8 g of a brown

colored solid catalyst component.

The solid catalyst component thus obtained contained 1.1% by weight of titanium atoms 7.8% by weight of magnesium atoms and 1.5% by weight of phthalic ester.

5 (C) Polymerization

Using the solid catalyst component obtained above, a polymerization of propylene was carried out under the same conditions as in Example 21 (A). The results were as follows: PP/Ti = 153,000, CXS = 2.5% by weight, BD = 0.42 g/ml.

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(D) Preparation of Biaxially Stretched Film

Using the polymer obtained in (C), a biaxially stretched film was prepared in the same manner as in Example 25 (B). Microscopic examination of this film, revealed 43 fish eyes per 1 cm<sup>2</sup>.

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Since in this experiment silica gel was used as the carrier, a larger number of fish eyes were formed in the film than in the film of Example 25.

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Table 1

|                          | Step 1                                     |                                     |                                  |                          |                   |
|--------------------------|--------------------------------------------|-------------------------------------|----------------------------------|--------------------------|-------------------|
|                          | (A)<br>Solid catalyst<br>component<br>(mg) | (B)<br>Triethyl-<br>aluminum<br>(g) | (C)<br>Electron donor<br>(g)     | Temper-<br>ature<br>(°C) | Time<br>(minutes) |
| Example 1                | 564.0                                      | 0.5                                 | Phenyltrimethoxy-<br>silane 0.13 | 75                       | 15                |
| Comparative<br>Example 1 | 297.0                                      | "                                   | "                                | "                        | 10                |
| " 2                      | 103.2                                      | "                                   | "                                | "                        | "                 |
| " 3                      | 31.8                                       | "                                   | "                                | "                        | "                 |
| " 4*)                    | 32.4                                       | "                                   | Methyl p-toluate<br>0.2          | "                        | "                 |
| Example 2                | 282.9                                      | "                                   | Phenyltrimethoxy-<br>silane 0.13 | "                        | "                 |
| " 3                      | 377.0                                      | "                                   | "                                | "                        | 15                |
| " 4                      | 372.4                                      | "                                   | "                                | "                        | 10                |

Note) Charges in step 1: C<sub>3</sub> 1.3 kg, H<sub>2</sub> <sup>0.52 bar</sup>(0.53 kg/cm<sup>2</sup>); charge in step 2: H<sub>2</sub> <sup>0.074 bar</sup>0.075(kg/cm<sup>2</sup>)  
 [(1) <sup>0.3 bar</sup>(0.3 kg/cm<sup>2</sup>), (2) <sup>0.2 bar</sup>(0.2 kg/cm<sup>2</sup>)]

\*) The catalyst entirely lost its activity in the course of step 2.

Table 1 (Cont'd.)

| Step 2                                                           |                     |                                            |                   |
|------------------------------------------------------------------|---------------------|--------------------------------------------|-------------------|
| C <sub>2</sub> '/ $\alpha$ -Olefin<br>composition<br>(% by vol.) | Temperature<br>(°C) | Pressure<br>(bar/<br>kg/cm <sup>2</sup> G) | Time<br>(minutes) |
| C <sub>2</sub> '/C <sub>3</sub> '=50/50                          | 70                  | 11/10                                      | 420               |
| "                                                                | "                   | "                                          | 390               |
| "                                                                | "                   | "                                          | 400               |
| "                                                                | "                   | "                                          | 360               |
| "                                                                | "                   | "                                          | 240               |
| C <sub>2</sub> '/C <sub>3</sub> '=80/20                          | "                   | " (1)                                      | 540               |
| C <sub>2</sub> '/C <sub>3</sub> '=50/50                          | "                   | " (2)                                      | 480               |
| C <sub>2</sub> '/C <sub>4</sub> '=30/20                          | 75                  | 5/4                                        | 420               |

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Table 2

|                          | Quantity of<br>polymerization<br>(g) | PP/Ti<br>(g/g) | Production ratio<br>(Step 1/Step 2)<br>(by wt.) | CXS in<br>Step 1<br>(% by wt.) | $[\eta]_P$ | $[\eta]_{EP}$        | $[\eta]_T$ |
|--------------------------|--------------------------------------|----------------|-------------------------------------------------|--------------------------------|------------|----------------------|------------|
| Example 1                | 643                                  | 228,000        | 15/85                                           | 3.8                            | 1.7        | 3.8                  | 3.5        |
| Comparative<br>Example 1 | 512                                  | 157,000        | 17/83                                           | 2.5                            | 2.3        | 3.8                  | 3.6        |
| " 2                      | 435                                  | 220,000        | 18/82                                           | 1.8                            | 2.2        | 3.7                  | 3.5        |
| " 3                      | 328                                  | 547,000        | 32/68                                           | 2.8                            | 2.3        | 3.0                  | 2.8        |
| " 4                      | 208                                  | 257,000        | 54/46                                           | 4.4                            | 2.4        | 3.9                  | 3.1        |
| Example 2                | 368                                  | 260,000        | 25/75                                           | 3.7                            | 2.0        | 3.5                  | 3.1        |
| " 3                      | 205                                  | 109,000        | 20/80                                           | 3.5                            | 1.7        | 2.6                  | 2.4        |
| " 4                      | 260                                  | 140,000        | 27/73                                           | 4.0                            | 2.2        | $[\eta]_{EB}$<br>4.1 | 3.6        |

(to be cont'd.)

Table 2 (Cont'd.)

| C <sub>2</sub> ' content<br>in Step 2<br>(% by wt.) | Adhesive force<br>of polymer<br>particle<br>(N/cm <sup>2</sup> / g/cm <sup>2</sup> ) | State of<br>autoclave                      |
|-----------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------|
| 48                                                  | 27/2.8                                                                               | Adhesion of<br>polymer<br>unnoticeable     |
| 46                                                  | 76/1.7                                                                               | "                                          |
| 47                                                  | 82/8.4                                                                               | "                                          |
| 47                                                  | Unmeasurable                                                                         | Adhesion of<br>polymer particle<br>noticed |
| 48                                                  | "                                                                                    | "                                          |
| 25                                                  | 21/2.1                                                                               | Adhesion of<br>polymer<br>unnoticeable     |
| 43                                                  | 47/4.8                                                                               | "                                          |
| 77                                                  | 24/2.4                                                                               | "                                          |

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Table 3

|                          | (A)<br>Solid catalyst<br>component<br>(mg) | Step 1                              |                                                    |                          |                   |
|--------------------------|--------------------------------------------|-------------------------------------|----------------------------------------------------|--------------------------|-------------------|
|                          |                                            | (B)<br>Triethyl-<br>aluminum<br>(g) | Electron donor:<br>Phenyltrimethoxy-<br>silane (g) | Temper-<br>ature<br>(°C) | Time<br>(minutes) |
| Example 5                | 313.2                                      | 0.5                                 | 0.13                                               | 60                       | 50                |
| Comparative<br>Example 5 | 127.0                                      | "                                   | "                                                  | "                        | 25                |
| " 6                      | 359.0                                      | "                                   | "                                                  | "                        | 15                |
| Example 6                | 421.3                                      | "                                   | "                                                  | "                        | 40                |
| " 7                      | 378.5                                      | "                                   | None                                               | "                        | 40                |
| " 8                      | 413.7                                      | "                                   | None                                               | "                        | 45                |
| Comparative<br>Example 7 | 144.0                                      | "                                   | None                                               | "                        | 30                |
| Example 9                | 302.8                                      | "                                   | 0.13                                               | "                        | 45                |
| " 10                     | 513.4                                      | "                                   | "                                                  | "                        | 40                |
| " 11                     | 370.5                                      | "                                   | "                                                  | "                        | 45                |

Note) Step 1: Partial pressure of  $H_2$ :  $\overset{4 \text{ bar}}{(3.0 \text{ kg/cm}^2 \text{G})}$ ; (to be cont'd.)  
total pressure:  $\overset{21 \text{ bar}}{(20 \text{ kg/cm}^2 \text{G})}$

Table 3 (Cont'd)

| Step 2                                                           |                     |                                                                            |                                                     |                   |
|------------------------------------------------------------------|---------------------|----------------------------------------------------------------------------|-----------------------------------------------------|-------------------|
| C <sub>2</sub> '/ $\alpha$ -Olefin<br>composition<br>(% by vol.) | Temperature<br>(°C) | Partial<br>pressure<br>of H <sub>2</sub><br>(bar/<br>kg/cm <sup>2</sup> G) | Total<br>pressure<br>(bar/<br>kg/cm <sup>2</sup> G) | Time<br>(minutes) |
| C <sub>2</sub> '/C <sub>3</sub> '=50/50                          | 70                  | 1.074 / 0.075                                                              | 11/10                                               | 90                |
| "                                                                | "                   | "                                                                          | "                                                   | 30                |
| "                                                                | "                   | "                                                                          | "                                                   | 60                |
| "                                                                | "                   | "                                                                          | "                                                   | 195               |
| "                                                                | 40                  | 1.05 / 0.05                                                                | "                                                   | 80                |
| "                                                                | "                   | "                                                                          | "                                                   | 120               |
| "                                                                | 30                  | "                                                                          | "                                                   | 100               |
| C <sub>2</sub> '/C <sub>3</sub> '=85/15                          | 70                  | 1.074 / 0.075                                                              | "                                                   | 210               |
| " =50/50                                                         | "                   | "                                                                          | "                                                   | 90                |
| C <sub>2</sub> '/C <sub>4</sub> '=80/20                          | 75                  | "                                                                          | "                                                   | 420               |

Table 4

|                          | Quantity of<br>polymerization<br>(g) | P/cat<br>(g/g) | Production ratio<br>(Step 1/Step 2)<br>(by wt.) | $[\eta]_E$ | $[\eta]_{EP}$        | $[\eta]_T$ |
|--------------------------|--------------------------------------|----------------|-------------------------------------------------|------------|----------------------|------------|
| Example 5                | 338                                  | 1,080          | 15/85                                           | 1.7        | 3.1                  | 2.9        |
| Comparative<br>Example 5 | 199                                  | 1,570          | 24/76                                           | 2.6        | 3.4                  | 3.2        |
| " 6                      | 397                                  | 1,110          | 13/87                                           | 2.3        | 3.1                  | 3.0        |
| Example 6                | 380                                  | 900            | 11/89                                           | 2.4        | 2.9                  | 2.9        |
| " 7                      | 450                                  | 1,190          | 10/90                                           | 2.4        | 1.9                  | 2.0        |
| " 8                      | 422                                  | 1,020          | 10/90                                           | 2.4        | 1.8                  | 1.8        |
| Comparative<br>Example 7 | 350                                  | 2,430          | 10/90                                           | 2.6        | 2.0                  | 2.1        |
| Example 9                | 478                                  | 1,580          | 11/89                                           | 2.0        | 4.1                  | 3.9        |
| " 10                     | 469                                  | 910            | 13/87                                           | 2.5        | 2.9                  | 2.8        |
| " 11                     | 456                                  | 1,230          | 15/85                                           | 1.8        | $[\eta]_{EB}$<br>3.0 | 2.8        |

(to be cont'd.)

Table 4 (Cont'd.)

| C <sub>2</sub> content<br>in Step 2<br>(% by wt.) | Adhesive force<br>of polymer<br>particles<br>(N/cm <sup>2</sup> / g/cm <sup>2</sup> ) | State of<br>autoclave                      |
|---------------------------------------------------|---------------------------------------------------------------------------------------|--------------------------------------------|
| 48                                                | 41/4.2                                                                                | Adhesion of<br>polymer<br>unnoticeable     |
| 46                                                | Unmeasurable                                                                          | Adhesion of<br>polymer particle<br>noticed |
| 48                                                | "                                                                                     | "                                          |
| 47                                                | 24/2.4                                                                                | "                                          |
| 49                                                | 31/3.2                                                                                | "                                          |
| 47                                                | 26/2.6                                                                                | "                                          |
| 47                                                | Unmeasurable                                                                          | "                                          |
| 79                                                | 34/3.5                                                                                | "                                          |
| 47                                                | 49/5.0                                                                                | "                                          |
| 80                                                | 43/4.4                                                                                | "                                          |

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Table 5

|                          | (A)<br>Solid catalyst<br>component<br>(mg) | (B)<br>Triethyl-<br>aluminum<br>(g) | Electron<br>donor:<br>Phenyltrimethoxy-<br>silane (g) | C <sub>2</sub> '/ $\alpha$ -Olefin<br>composition<br>(% by vol.) | Temper-<br>ature<br>(°C) |
|--------------------------|--------------------------------------------|-------------------------------------|-------------------------------------------------------|------------------------------------------------------------------|--------------------------|
| Example 12               | 418.2                                      | 0.5                                 | 0.13                                                  | C <sub>2</sub> '/C <sub>3</sub> '=50/50                          | 60                       |
| Comparative<br>Example 8 | 144.1                                      | "                                   | "                                                     | "                                                                | "                        |
| " 9                      | 237.5                                      | "                                   | "                                                     | "                                                                | "                        |
| Example 13               | 310.0                                      | "                                   | "                                                     | "                                                                | 75                       |
| " 14                     | 271.5                                      | "                                   | "                                                     | C <sub>2</sub> '/C <sub>3</sub> '=70/30                          | "                        |
| " 15                     | 378.5                                      | "                                   | "                                                     | C <sub>2</sub> '/C <sub>3</sub> '=50/50                          | 60                       |
| " 16                     | 315.0                                      | "                                   | None                                                  | "                                                                | "                        |
| " 17                     | 331.0                                      | "                                   | 0.13                                                  | (*)<br>C <sub>2</sub> '/C <sub>3</sub> '=50/50                   | "                        |
| " 18                     | 408.3                                      | "                                   | "                                                     | C <sub>2</sub> '/C <sub>4</sub> '=80/20                          | "                        |

(to be cont'd.)

(\*) Polymerization in the presence of 1,9-decadiene

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Table 5 (Cont'd.)

| Partial pressure of H <sub>2</sub> (bar/kg/cm <sup>2</sup> G) | Total pressure (bar/kg/cm <sup>2</sup> G) | Time (minutes) |
|---------------------------------------------------------------|-------------------------------------------|----------------|
| 1.60/0.61                                                     | 11/10                                     | 50             |
| "                                                             | "                                         | 60             |
| "                                                             | "                                         | 45             |
| 1.47/0.48                                                     | "                                         | 60             |
| 1.42/0.43                                                     | "                                         | 90             |
| 2.03/1.03                                                     | "                                         | 30             |
| 1.10/0.10                                                     | "                                         | 60             |
| 1.40/0.41                                                     | "                                         | "              |
| 1.33/0.34                                                     | 6/5                                       | 120            |

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Table 6

|                          | Quantity of<br>polymer<br>(g) | P/cat<br>(g/g) | [ $\eta$ ] | C <sub>2</sub> content<br>(% by wt.) | 1,9-Decadiene<br>content<br>(% by wt.) | Adhesive<br>force of<br>polymer<br>particles<br>(g/cm <sup>2</sup> ) | State of<br>autoclave                    |
|--------------------------|-------------------------------|----------------|------------|--------------------------------------|----------------------------------------|----------------------------------------------------------------------|------------------------------------------|
| Example 12               | 151                           | 360            | 2.6        | 77.0                                 | -                                      | 2.1                                                                  | Adhesion of<br>polymer un-<br>noticeable |
| Comparative<br>Example 8 | 160                           | 1,110          | 2.7        | 72.8                                 | -                                      | Un-<br>measurable                                                    | Polymer mass<br>formed                   |
| " 9                      | 160                           | 670            | 2.9        | 67.0                                 | -                                      | "                                                                    | "                                        |
| Example 13               | 151                           | 490            | 2.1        | 61.0                                 | -                                      | 3.2                                                                  | Adhesion of<br>polymer<br>unnoticeable   |
| " 14                     | 111                           | 410            | 3.2        | 82.3                                 | -                                      | 2.4                                                                  | "                                        |
| " 15                     | 115                           | 300            | 1.9        | 54.7                                 | -                                      | 3.4                                                                  | "                                        |
| " 16                     | 175                           | 560            | 2.1        | 33.6                                 | -                                      | 4.0                                                                  | "                                        |
| " 17                     | 140                           | 420            | 2.5        | 61.6                                 | 9.7                                    | 5.7                                                                  | "                                        |
| " 18                     | 93                            | 230            | 2.3        | 79.6                                 | -                                      | 4.1                                                                  | "                                        |

Table 7

|                             | Example 21                     | Comparative<br>Example 12 | Example 22 | Example 23 | Example 24 |
|-----------------------------|--------------------------------|---------------------------|------------|------------|------------|
| Mesh size ( $\mu\text{m}$ ) | Cumulative fraction (% by wt.) |                           |            |            |            |
| 3360                        | 100.0                          | 100.0                     | 100.0      | 100.0      | 100.0      |
| 2830                        | 100.0                          | 100.0                     | 99.7       | 100.0      | 100.0      |
| 2380                        | 100.0                          | 100.0                     | 98.9       | 100.0      | 100.0      |
| 2000                        | 100.0                          | 100.0                     | 93.2       | 100.0      | 100.0      |
| 1680                        | 99.9                           | 100.0                     | 79.1       | 99.9       | 100.0      |
| 1410                        | 97.6                           | 100.0                     | 60.8       | 98.0       | 100.0      |
| 1190                        | 80.4                           | 99.8                      | 44.5       | 80.8       | 100.0      |
| 1000                        | 27.7                           | 97.3                      | 32.6       | 35.7       | 100.0      |
| 710                         | 0.8                            | 88.4                      | 14.7       | 0.1        | 100.0      |
| 590                         | 0.1                            | 35.3                      | 5.8        | 0.0        | 99.4       |
| 500                         | 0.0                            | 19.8                      | 0.6        | 0.0        | 71.6       |
| 420                         | 0.0                            | 13.9                      | 0.2        | 0.0        | 32.6       |

(to be cont'd.)

Table 7 (Cont'd.)

|             |      |      |      |      |      |
|-------------|------|------|------|------|------|
| 350         | 0.0  | 9.5  | 0.1  | 0.0  | 13.9 |
| 297         | 0.0  | 4.0  | 0.0  | 0.0  | 1.5  |
| 250         | 0.0  | 2.0  | 0.0  | 0.0  | 0.4  |
| 177         | 0.0  | 0.9  | 0.0  | 0.0  | 0.1  |
| 125         | 0.0  | 0.3  | 0.0  | 0.0  | 0.0  |
| Pan (< 125) | 0.0  | 0.1  | 0.0  | 0.0  | 0.0  |
| BD (g/ml)   | 0.43 | 0.30 | 0.35 | 0.45 | 0.34 |

As has been mentioned above, the use of the catalyst system of the present invention brings about the following effects:

(1) Since the catalyst system has a very high catalytic activity per one titanium atom, there can be obtained an  $\alpha$ -olefin polymer containing only very small quantities of halogen and titanium, closely relating to the colorizability, stability of polymer and corrosiveness of apparatus, without any particular

procedure for removing the catalyst residue. That is, the invention makes the apparatus for removal of catalyst residue unnecessary and reduces the production cost of  $\alpha$ -olefin polymer.

(2) When the catalyst of the present invention is used for the purpose of producing crystalline polymers, since the catalyst system of the invention forms only a very small quantity of amorphous polymer as by-product, it can produce  $\alpha$ -olefin polymers with excellent mechanical properties without removing the amorphous polymer.

(3) The use of the catalyst system of the invention enables one to produce an  $\alpha$ -olefin polymer having a very high bulk density, which can decrease the size of the production plant and achieves a very high productivity.

(4) In the catalyst system of the invention, the shape of porous polymer beads is by the shape of solid catalyst. This means that the shape and size of  $\alpha$ -olefin polymer can easily be controlled by varying the shape and size of polymer beads, because they have an analogous relationship.

(5) The use of the catalyst system of the invention enables one to minimize the quantity of fine powder in the  $\alpha$ -olefin polymer, owing to which the clogging troubles in the piping caused by fine powder can be prevented.

(6) The use of the catalyst system of the invention enables one to achieve the above-mentioned effects (4) and (5) without contaminating the  $\alpha$ -olefin polymer with inorganic oxide deteriorating the product quality by fish eyes for example.

(7) By combining the catalyst system of the invention with a gas phase polymerization process, granular elastomers and granular thermoplastic elastomers can be produced with a high efficiency and a high stability, owing to which the production cost can be much lower than in prior processes.

(8) The catalyst system of the invention enables one to obtain elastomers and thermoplastic elastomers in a granular form, which facilitates the procedures of molding and processing.

## 25 Claims

1. A solid catalyst component for  $\alpha$ -olefin polymerization containing as catalyst components at least titanium, magnesium and chlorine which are impregnated into an organic porous polymer carrier having a mean particle diameter of 5 to 1,000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to  $5,000 \cdot 10^{-10}$  m (100 to 5,000 Å).
2. A solid catalyst component according to Claim 1, wherein the atomic ratio of titanium/magnesium and chlorine/magnesium are 0.01-0.8 and 1.8-10, respectively.
3. A solid catalyst component according to Claim 1, wherein the amount of the catalyst component impregnated into the organic porous polymer carrier is 1-70% by weight in the solid catalyst component.
4. A solid catalyst component according to Claim 1, wherein the organic porous polymer carrier is a porous polymer bead selected from the group consisting of polystyrenes, polyvinyl chlorides, polyolefins, and polyacrylonitriles.
5. A solid catalyst component according to Claim 1, which is a solid catalyst component containing a trivalent titanium compound obtained by reducing a titanium compound represented by the general formula  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (wherein  $\text{R}^1$  is a hydrocarbon group of 1 to 20 carbon atoms, X is a halogen atom; and n is a number satisfying  $0 < n \leq 4$ ) with an organomagnesium compound in the presence of an organic porous polymer carrier having a mean particle diameter of 5 to 1000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to  $5,000 \cdot 10^{-10}$  m (100 to 5,000 Å), or in the co-presence of said organic porous polymer carrier and an organo silicone compound having a Si-O bond to obtain a solid product, treating the solid product with an ester compound, and a mixture of an ether compound and titanium tetrachloride.
6. A solid catalyst component according to Claim 1, which is a solid catalyst component containing a trivalent titanium compound obtained by reducing a titanium compound represented by the general formula  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (wherein  $\text{R}^1$  is a hydrocarbon group of 1 to 20 carbon atoms, X is a halogen atom; and n is a number satisfying  $0 < n \leq 4$ ) with an organomagnesium compound in the presence of an organic porous polymer carrier having a mean particle diameter of 5 to 1000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to  $5,000 \cdot 10^{-10}$  m (100 to 5,000 Å), or in the co-presence of



procedure for removing the catalyst residue. That is, the invention makes the apparatus for removal of catalyst residue unnecessary and reduces the production cost of  $\alpha$ -olefin polymer.

(2) When the catalyst of the present invention is used for the purpose of producing crystalline polymers, since the catalyst system of the invention forms only a very small quantity of amorphous polymer as by-product, it can produce  $\alpha$ -olefin polymers with excellent mechanical properties without removing the amorphous polymer.

(3) The use of the catalyst system of the invention enables one to produce an  $\alpha$ -olefin polymer having a very high bulk density, which can decrease the size of the production plant and achieves a very high productivity.

(4) In the catalyst system of the invention, the shape of porous polymer beads is by the shape of solid catalyst. This means that the shape and size of  $\alpha$ -olefin polymer can easily be controlled by varying the shape and size of polymer beads, because they have an analogous relationship.

(5) The use of the catalyst system of the invention enables one to minimize the quantity of fine powder in the  $\alpha$ -olefin polymer, owing to which the clogging troubles in the piping caused by fine powder can be prevented.

(6) The use of the catalyst system of the invention enables one to achieve the above-mentioned effects (4) and (5) without contaminating the  $\alpha$ -olefin polymer with inorganic oxide deteriorating the product quality by fish eyes for example.

(7) By combining the catalyst system of the invention with a gas phase polymerization process, granular elastomers and granular thermoplastic elastomers can be produced with a high efficiency and a high stability, owing to which the production cost can be much lower than in prior processes.

(8) The catalyst system of the invention enables one to obtain elastomers and thermoplastic elastomers in a granular form, which facilitates the procedures of molding and processing.

## Claims

1. A solid catalyst component for  $\alpha$ -olefin polymerization containing as catalyst components at least titanium, magnesium and chlorine which are impregnated into an organic porous polymer carrier having a mean particle diameter of 5 to 1,000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to 5,000  $\cdot 10^{-10}$  m (100 to 5,000  $\text{\AA}$ ).
2. A solid catalyst component according to Claim 1, wherein the atomic ratio of titanium/magnesium and chlorine/magnesium are 0.01-0.8 and 1.8-10, respectively.
3. A solid catalyst component according to Claim 1, wherein the amount of the catalyst component impregnated into the organic porous polymer carrier is 1-70% by weight in the solid catalyst component.
4. A solid catalyst component according to Claim 1, wherein the organic porous polymer carrier is a porous polymer bead selected from the group consisting of polystyrenes, polyvinyl chlorides, polyolefins, and polyacrylonitriles.
5. A solid catalyst component according to Claim 1, which is a solid catalyst component containing a trivalent titanium compound obtained by reducing a titanium compound represented by the general formula  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (wherein  $\text{R}^1$  is a hydrocarbon group of 1 to 20 carbon atoms, X is a halogen atom; and n is a number satisfying  $0 < n \leq 4$ ) with an organomagnesium compound in the presence of an organic porous polymer carrier having a mean particle diameter of 5 to 1000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to 5,000  $\cdot 10^{-10}$  m (100 to 5,000  $\text{\AA}$ ), or in the co-presence of said organic porous polymer carrier and an organo silicone compound having a Si-O bond to obtain a solid product, treating the solid product with an ester compound, and a mixture of an ether compound and titanium tetrachloride.
6. A solid catalyst component according to Claim 1, which is a solid catalyst component containing a trivalent titanium compound obtained by reducing a titanium compound represented by the general formula  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (wherein  $\text{R}^1$  is a hydrocarbon group of 1 to 20 carbon atoms, X is a halogen atom; and n is a number satisfying  $0 < n \leq 4$ ) with an organomagnesium compound in the presence of an organic porous polymer carrier having a mean particle diameter of 5 to 1000  $\mu\text{m}$  and a pore volume of 0.1 ml/g or above at a pore radius of 100 to 5,000  $\cdot 10^{-10}$  m (100 to 5,000  $\text{\AA}$ ), or in the co-presence of



said organic porous polymer carrier and an organo silicone compound having a Si-O bond to obtain a solid product, treating the solid product with a mixture of an ether compound and titanium tetrachloride.

- 5 7. A solid catalyst component according to Claim 5 or 6, wherein the hydrocarbon group  $R^1$  of the titanium compound represented by the general formula  $Ti(OR^1)_nX_{4-n}$  is an alkyl groups having 2 to 18 carbon atoms or an aryl groups having 6 to 18 carbon atoms.
- 10 8. A solid catalyst component according to Claim 5 or 6, wherein the X of the titanium compound represented by the general formula  $Ti(OR^1)_nX_{4-n}$  is chlorine.
- 15 9. A solid catalyst component according to Claim 5 or 6, wherein the n of the titanium compound represented by the general formula  $Ti(OR^1)_nX_{4-n}$  is a number satisfying  $2 \leq n \leq 4$ .
- 20 10. A solid catalyst component according to Claim 5 or 6, wherein the organomagnesium compound is a Grignard compound represented by the general formula  $R'MgX$  (wherein  $R'$  is a hydrocarbon group of 1 to 20 carbon atoms and X is a halogen atom), or a dialkyl magnesium compound or a diaryl magnesium compound both represented by the general formula  $R''R'''Mg$  (wherein  $R''$  and  $R'''$  are each a hydrocarbon group having 1 to 20 carbon atoms).
- 25 11. A solid catalyst component according to Claim 5, wherein the ester compound is mono or polyvalent carboxylic acid ester.
- 30 12. A solid catalyst component according to Claim 5 or 6, wherein the ether compound is an dialkyl ether.
- 35 13. A solid catalyst component according to Claim 5 or 6, wherein the organosilicone compound having a Si-O bond is represented by the following general formula:  

$$Si(OR^3)_mR^{4-4-m},$$

$$R^5(R^6_2SiO)_pSiR^7_3 \text{ or}$$

$$(R^8_2SiO)_q$$

(wherein  $R^3$  is a hydrocarbon group having 1 to 20 carbon atoms;  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are each a hydrocarbon group having 1 to 20 carbon atoms or a hydrogen atom; m is a number satisfying  $0 < m \leq 4$ ; p is an integer of 1 to 1,000; and q is an integer of 2 to 1,000).
- 40 14. A solid catalyst component according to Claim 5 or 6, wherein the organosilicone compound having a Si-O bond is an alkoxysilane compound represented by the general formula  $Si(OR^3)_mR^{4-4-m}$ , in which m is a number satisfying  $1 \leq m \leq 4$ .
- 45 15. A solid catalyst component according to Claim 5 or 6, wherein the organosilicone compound having a Si-O bond is used in an amount of 1 to 50 in terms of the atomic ratio of silicon atoms to titanium atoms in titanium compound.
- 50 16. A solid catalyst component according to Claim 5 or 6, wherein the organomagnesium compound is used in an amount of 0.1 to 10 in terms of the atomic ratio of the sum of titanium atoms and silicon atoms to magnesium atoms.
- 55 17. A solid catalyst component according to Claim 5 or 6, wherein the reduction is conducted at a temperature of  $-50^\circ$  to  $70^\circ$  C.
18. A solid catalyst component according to Claim 5, wherein the ester compound is used in an amount of 0.1 to 50 moles per 1 mole of titanium atom in the solid product.
19. A solid catalyst component according to Claim 5 or 6, wherein the ether compound is used in an amount of 0.1 to 100 moles per 1 mole of titanium atom in the solid product.
20. A solid catalyst component according to Claim 5 or 6, wherein titanium tetrachloride is used in an amount of 2 to 2,000 moles per 1 mole of titanium atom in the solid product and in an amount of 1 to



100 moles per mole of ether compound.

21. A solid catalyst component according to Claim 5, wherein the solid product is treated with an ester compound in a diluent at a temperature of  $-50^{\circ}$  to  $150^{\circ}\text{C}$ .
- 5 22. A solid catalyst component according to Claim 21, wherein the diluent is an aromatic hydrocarbon or a halogenated hydrocarbon.
- 10 23. A solid catalyst component according to Claim 5, wherein the ester-treated solid product is treated with a mixture of an ether compound and titanium tetrachloride in a slurry state using a solvent at  $30^{\circ}$  to  $150^{\circ}\text{C}$ .
- 15 24. A solid catalyst component according to Claim 23, wherein the solvent is an aliphatic hydrocarbon, aromatic hydrocarbon, alicyclic hydrocarbon or a halogenated hydrocarbon.
- 20 25. A catalyst system for  $\alpha$ -olefin polymerization comprising at least
  - (A) a solid catalyst component according to Claim 1 containing as catalyst components at least titanium, magnesium and chlorine which are impregnated into an organic porous polymer carrier having a mean particle diameter of 5 to  $1,000\text{ }\mu\text{m}$  and a pore volume of  $0.1\text{ ml/g}$  or above at a pore radius of  $100\text{ to }5,000 \cdot 10^{-10}\text{ m}$  ( $100\text{ to }5,000\text{ }\text{\AA}$ ), and
  - (B) an organoaluminum compound.
- 25 26. A catalyst system according to Claim 25, wherein the solid catalyst component is a solid catalyst component containing a trivalent titanium compound obtained by reducing a titanium compound represented by the general formula  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (wherein  $\text{R}^1$  is a hydrocarbon group of 1 to 20 carbon atoms, X is a halogen atom, and n is a number satisfying  $0 < n \leq 4$ ) with an organo magnesium compound in the presence of an organic porous polymer carrier having a mean particle diameter of 5 to  $1,000\text{ }\mu\text{m}$  and a pore volume of  $0.1\text{ ml/g}$  or above at a pore radius of  $100\text{ to }5,000 \cdot 10^{-10}\text{ m}$  ( $100\text{ to }5,000\text{ }\text{\AA}$ ), or in the co-presence of said organic porous polymer carrier and an organo silicone compound having a Si-O bond to obtain a solid product, treating the solid product with an ester compound, and a mixture of an ether compound and titanium tetrachloride.
- 30 27. A catalyst system according to Claim 25, wherein the solid catalyst component is a solid catalyst component containing a trivalent titanium compound obtained by reducing a titanium compound represented by the general formula  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (wherein  $\text{R}^1$  is a hydrocarbon group of 1 to 20 carbon atoms, X is a halogen atom, and n is a number satisfying  $0 < n \leq 4$ ) with an organo magnesium compound in the presence of an organic porous polymer carrier having a mean particle diameter of 5 to  $1,000\text{ }\mu\text{m}$  and a pore volume of  $0.1\text{ ml/g}$  or above at a pore radius of  $100\text{ to }5,000 \cdot 10^{-10}\text{ m}$  ( $100\text{ to }5,000\text{ }\text{\AA}$ ), or in the co-presence of said organic porous polymer carrier and an organo silicone compound having a Si-O bond to obtain a solid product, treating the solid product with a mixture of an ether compound and titanium tetrachloride.
- 35 28. A catalyst system for  $\alpha$ -olefin polymerization according to Claim 25, wherein the organoaluminum compound (B) is a compound having at least one Al-C bond within the molecule and is represented by the general formula
 
$$\text{R}^9_\gamma\text{AlY}_{3-\gamma} \text{ or } \text{R}^{10}\text{R}^{11}\text{Al-O-AlR}^{12}\text{R}^{13}$$

(wherein  $\text{R}^9$ ,  $\text{R}^{10}$ ,  $\text{R}^{11}$ ,  $\text{R}^{12}$  and  $\text{R}^{13}$  are each a hydrocarbon group having 1 to 8 carbon atoms; Y is a halogen atom, a hydrogen atom or an alkoxy group; and  $\gamma$  is a number of satisfying  $2 \leq \gamma \leq 3$ ).
- 40 29. A catalyst system for  $\alpha$ -olefin polymerization according to Claim 28, wherein the organoaluminum compound is a trialkylaluminum, a mixture of a trialkylaluminum and a dialkylaluminum halide, or an alkyl alumoxane.
- 45 30. A catalyst system according to Claim 25, wherein an electron donor (C) is further added.
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31. A catalyst system according to Claim 30, wherein the electron donor (C) is a compound selected from the group consisting of organo silicon compounds having a Si-OR<sup>2</sup> bond (R<sup>2</sup> represents a hydrocarbon residue having 1 to 20 carbon atoms) or a Si-N-C bond, aromatic carboxylic ester compounds and sterically hindered amines.

32. A catalyst system according to Claim 31, wherein the electron donor is an organo silicon compound.

33. A catalyst system according to Claim 32, wherein the organosilicon compound is an alkoxysilane compound represented by the general formula R<sup>14</sup><sub>t</sub>Si(OR<sup>2</sup>)<sub>4-t</sub> (where R<sup>14</sup> and R<sup>2</sup> each represents a hydrocarbon residue having 1 to 20 carbon atoms, and t represents a number satisfying 0 ≤ t ≤ 3).

34. A catalyst system according to Claim 30, wherein the electron donor is used in an amount of 0.01 to 5 moles per 1 mole of the aluminum atom in the organoaluminum compound (B).

35. A process for producing a granular thermoplastic elastomer and a granular elastomer which comprises polymerizing an α-olefin or copolymerizing α-olefin by the use of a catalyst system according to Claim 25 comprising at least

a solid catalyst component (A) containing as catalyst components at least titanium, magnesium and chlorine which are impregnated into an organic porous polymer carrier having a mean particle diameter of 5 to 1,000 μm and a pore volume of 0.1 ml/g or above at a pore radius of 100 to 5,000 · 10<sup>-10</sup> m (100 to 5,000 Å) and

an organoaluminum compound (B).

36. A process according to Claim 35, wherein the process comprises, in the first step, preparing an isotactic polypropylene by a polymerization reaction in liquefied propylene and/or in the gas phase, followed by, in the second step, preparing an ethylene-α-olefin random copolymer in the gas phase so that the ethylene content in the copolymer formed in the second step reaches 5 to 95% by weight and its intrinsic viscosity in tetralin at 135 °C comes to 0.3 to 10 and the weight of the copolymer formed in the second step comes to 60 to 97% by weight based on the total weight of the polymers.

37. A process according to Claim 35, wherein the process comprises, in the first step, polymerising ethylene in a slurry state in a propane solvent or a butane solvent or polymerizing ethylene in gas phase, followed by, in the second step, preparing an ethylene-α-olefin random copolymer by a polymerization reaction in the gas phase so that the ethylene content in the copolymer formed in the second step reaches 5 to 95% by weight and its intrinsic viscosity in tetralin at 135 °C comes to 0.3 to 10 and the weight of the copolymer formed in the second step comes to 60 to 97% by weight based on the total weight of the polymers.

38. A process according to Claim 35, wherein the process comprises carrying out a random copolymerization of ethylene and α-olefin in the gas phase so that the ethylene content in the copolymer thus formed reaches 5 to 95% by weight and its intrinsic viscosity in tetralin at 135 °C comes to 0.3 to 10.

39. A process according to Claim 35, wherein the catalyst system further contains an electron donor (C).

#### Patentansprüche

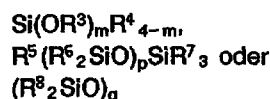
1. Fester Katalysatorbestandteil zur α-Olefin-Polymerisation, enthaltend als Katalysatorbestandteile mindestens Titan, Magnesium und Chlor, die in einen organischen porösen Polymerträger imprägniert sind, der einen durchschnittlichen Teilchendurchmesser von 5 bis 1000 μm und ein Porenvolumen von 0,1 ml/g oder darüber, bei einem Porenradius von 100 bis 5000 x 10<sup>-10</sup> m (100 bis 5000 Å), aufweist.

2. Fester Katalysatorbestandteil nach Anspruch 1, wobei das Atomverhältnis von Titan/Magnesium und Chlor/Magnesium 0,01 bis 0,8 bzw. 1,8 bis 10 beträgt.

3. Fester Katalysatorbestandteil nach Anspruch 1, wobei die Menge des Katalysatorbestandteils, der in den organischen porösen Polymerträger imprägniert ist, 1 bis 70 Gew.-% im festen Katalysatorbestandteil ausmacht.



4. Fester Katalysatorbestandteil nach Anspruch 1, wobei der organische poröse Polymerträger eine poröse Polymerperle ausgewählt aus der Gruppe Polystyrole, Polyvinylchloride, Polyolefine und Polyacrylnitrile, ist.
5. Fester Katalysatorbestandteil nach Anspruch 1, nämlich ein fester Katalysatorbestandteil, bestehend aus einer dreiwertigen Titanverbindung, erhältlich durch Reduzieren einer Titanverbindung wiedergegeben durch die allgemeine Formel  $Ti(OR^1)_nX_{4-n}$  (in der  $R^1$  einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet, X ein Halogenatom darstellt und n eine Zahl bedeutet, die der Ungleichung  $0 < n \leq 4$  genügt), mit einer Organomagnesiumverbindung in Gegenwart eines organischen porösen Polymerträgers mit einem durchschnittlichen Teilchendurchmesser von 5 bis 1000  $\mu m$  und einem Porenvolumen von 0,1 ml/g oder darüber, bei einem Porenradius von 100 bis  $5000 \times 10^{-10}$  m (100 bis 5000 Å) oder in gleichzeitiger Gegenwart des organischen porösen Polymerträgers und einer Organosiliciumverbindung mit einer Si-O-Bindung, unter Erhalt eines festen Produkts, Behandeln des festen Produkts mit einer Esterverbindung und einem Gemisch einer Etherverbindung und Titan-tetrachlorid.
6. Fester Katalysatorbestandteil nach Anspruch 1, nämlich ein fester Katalysatorbestandteil mit einer dreiwertigen Titanverbindung, erhältlich durch Reduzieren einer Titanverbindung, wiedergegeben durch die allgemeine Formel  $Ti(OR^1)_nX_{4-n}$ , (in der  $R^1$  einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet, X ein Halogenatom darstellt, und n eine Zahl bedeutet, die der Ungleichung  $0 < n \leq 4$  genügt) mit einer Organomagnesiumverbindung in Gegenwart eines organischen porösen Polymerträgers mit einem durchschnittlichen Teilchendurchmesser von 5 bis 1000  $\mu m$  und einem Porenvolumen von 0,1 ml/g oder darüber bei einem Porenradius von 100 bis  $5000 \cdot 10^{-10}$  m (100 bis 5000 Å) oder in gleichzeitiger Gegenwart des organischen porösen Polymerträgers und einer Organosiliciumverbindung mit einer Si-O-Bindung, unter Erhalt eines festen Produkts, Behandeln des festen Produkts mit einem Gemisch einer Etherverbindung und Titan-tetrachlorid.
7. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei der Kohlenwasserstoffrest  $R^1$  der Titanverbindung, wiedergegeben durch die allgemeine Formel  $Ti(OR^1)_nX_{4-n}$ , einen Alkylrest mit 2 bis 18 Kohlenstoffatomen oder einen Arylrest mit 6 bis 18 Kohlenstoffatomen bedeutet.
8. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei X in der Titanverbindung, wiedergegeben durch die allgemeine Formel  $Ti(OR^1)_nX_{4-n}$ , ein Chloratom ist.
9. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei n in der Titanverbindung, wiedergegeben durch die allgemeine Formel  $Ti(OR^1)_nX_{4-n}$ , eine Zahl ist, die der Ungleichung  $2 \leq n \leq 4$  genügt.
10. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Organomagnesiumverbindung eine Grignardverbindung, wiedergegeben durch die allgemeine Formel  $R^1RMgX$  (in der  $R^1$  einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet, und X ein Halogenatom darstellt) oder eine Dialkylmagnesiumverbindung oder eine Diarylmagnesiumverbindung, beide wiedergegeben durch die allgemeine Formel  $R''R'''Mg$  (in der  $R''$  und  $R'''$  jeweils einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeuten) darstellt.
11. Fester Katalysatorbestandteil nach Anspruch 5, wobei die Esterverbindung ein ein- oder mehrwertiger Carbonsäure- ester ist.
12. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Etherverbindung ein Dialkylether ist.
13. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Organosiliciumverbindung mit einer Si-O-Bindung, wiedergegeben wird durch die nachstehende allgemeine Formel:



(in der  $R^3$  einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet;  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  und  $R^8$  jeweils einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen oder ein Wasserstoffatom darstel-



len; m eine Zahl bedeutet, die der Ungleichung  $0 < m \leq 4$  genügt; p eine ganze Zahl von 1 bis 1000 darstellt und q eine ganze Zahl von 2 bis 1000 bedeutet).

- 5 14. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Organosiliciumverbindung mit einer Si-O-Bindung eine Alkoxysilanverbindung ist, wiedergegeben durch die allgemeine Formel  $\text{Si}(\text{OR}^3)_m\text{R}^4_{4-m}$ , in der m eine Zahl bedeutet, die der Ungleichung  $1 \leq m \leq 4$  genügt.
- 10 15. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Organosiliciumverbindung mit einer Si-O-Bindung in einer Menge von 1 bis 50, bezogen auf das Atomverhältnis der Siliciumatome zu den Titanatomen, in der Titanverbindung verwendet wird.
- 15 16. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Organomagnesiumverbindung in einer Menge von 0,1 bis 10, bezogen auf das Atomverhältnis der Summe der Titanatome und der Siliciumatome zu den Magnesiumatomen, verwendet wird.
- 20 17. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Reduktion bei einer Temperatur von  $-50^\circ\text{C}$  bis  $70^\circ\text{C}$  ausgeführt wird.
18. Fester Katalysatorbestandteil nach Anspruch 5, wobei die Esterverbindung in einer Menge von 0,1 bis 50 Mol pro Mol Titanatom in dem Festprodukt verwendet wird.
- 25 19. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei die Etherverbindung in einer Menge von 0,1 bis 100 Mol pro Mol Titanatom in dem Festprodukt verwendet wird.
- 20 20. Fester Katalysatorbestandteil nach Anspruch 5 oder 6, wobei Titan-tetrachlorid in einer Menge von 2 bis 2000 Mol pro 1 Mol Titanatom in dem Festprodukt und in einer Menge von 1 bis 100 Mol pro 1 Mol Etherverbindung verwendet wird.
- 30 21. Fester Katalysatorbestandteil nach Anspruch 5, wobei das Festprodukt mit einer Esterverbindung in einem Verdünnungsmittel bei einer Temperatur von  $-50^\circ\text{C}$  bis  $150^\circ\text{C}$  behandelt wird.
22. Fester Katalysatorbestandteil nach Anspruch 21, wobei das Verdünnungsmittel ein aromatischer Kohlenwasserstoff oder ein halogener Kohlenwasserstoff ist.
- 35 23. Fester Katalysatorbestandteil nach Anspruch 5, wobei das esterbehandelte Festprodukt mit einem Gemisch einer Etherverbindung und Titan-tetrachlorid im Aufschlammzustand unter Verwendung eines Lösungsmittels bei  $30^\circ\text{C}$  bis  $150^\circ\text{C}$  behandelt wird.
24. Fester Katalysatorbestandteil nach Anspruch 23, wobei das Lösungsmittel ein aliphatischer Kohlenwasserstoff, aromatischer Kohlenwasserstoff, alicyclischer Kohlenwasserstoff oder ein halogener Kohlenwasserstoff ist.
- 45 25. Katalysatorsystem zur  $\alpha$ -Olefin-Polymerisierung, umfassend Zumindest
  - (A) einen festen Katalysatorbestandteil nach Anspruch 1, enthaltend als Katalysatorbestandteile mindestens Titan, Magnesium und Chlor, die in einen organischen porösen Polymerträger imprägniert sind, der einen durchschnittlichen Teilchendurchmesser von 5 bis 1000  $\mu\text{m}$  und ein Porenvolumen von 0,1 ml/g oder darüber, bei einem Porenradius von 100 bis 5000  $\cdot 10^{-10}$  m (100 bis 5000 Å) aufweist, und
  - (B) eine Organoaluminiumverbindung.
- 50 26. Katalysatorsystem nach Anspruch 25, wobei der feste Katalysatorbestandteil ein fester eine dreiwertige Titanverbindung enthaltender Katalysatorbestandteil ist, erhältlich durch Reduktion einer Titanverbindung, wiedergegeben durch die allgemeine Formel  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (in der  $\text{R}^1$  einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet, X ein Halogenatom darstellt und n eine Zahl bedeutet, die der Ungleichung  $0 < n \leq 4$  genügt), mit einer Organomagnesiumverbindung in Gegenwart eines organischen porösen Polymerträgers mit einem durchschnittlichen Teilchendurchmesser von 5 bis 1000  $\mu\text{m}$  und einem Porenvolumen von 0,1 ml/g oder darüber, bei einem Porenradius von 100 bis 5000  $\cdot 10^{-10}$  m (100 bis 5000 Å), oder in gleichzeitiger Gegenwart des organischen porösen Polymerträgers und
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einer Organosiliciumverbindung mit einer Si-O-Bindung, unter Erhalt eines festen Produkts, Behandeln des festen Produkts mit einer Esterverbindung und einem Gemisch aus einer Etherverbindung und Titan-tetrachlorid.

- 5 27. Katalysatorsystem nach Anspruch 25, wobei der feste Katalysatorbestandteil ein fester eine dreiwertige Titanverbindung enthaltender Katalysatorbestandteil ist, erhältlich durch Reduktion einer Titanverbindung, wiedergegeben durch die allgemeine Formel  $Ti(OR^1)_nX_{4-n}$  (in der  $R^1$  einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet, X ein Halogenatom darstellt und n eine Zahl bedeutet, die der Ungleichung  $0 < n \leq 4$  genügt), mit einer Organomagnesiumverbindung in Gegenwart eines organischen porösen Polymerträgers mit einem durchschnittlichen Teilchendurchmesser von 5 bis 1000  $\mu m$  und einem Porenvolumen von 0,1 ml/g oder darüber, bei einem Porenradius von 100 bis  $5000 \cdot 10^{-10}$  m (100 bis 5000 Å) oder in gleichzeitiger Gegenwart des organischen porösen Polymerträgers und einer Organosiliciumverbindung mit einer Si-O-Bindung, unter Erhalt eines festen Produkts, Behandeln des festen Produkts mit einem Gemisch einer Etherverbindung und Titan-tetrachlorid.
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- 15 28. Katalysatorsystem zur  $\alpha$ -Olefin-Polymerisierung nach Anspruch 25, wobei die Organoaluminiumverbindung (B) eine Verbindung mit mindestens einer Al-C-Bindung im Molekül darstellt und wiedergegeben wird durch die allgemeine Formel
 

$$R^9_\gamma AlY_{3-\gamma} \text{ oder } R^{10}R^{11}Al-O-AlR^{12}R^{13}$$

(in der  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  und  $R^{13}$  jeweils einen Kohlenwasserstoffrest mit 1 bis 8 Kohlenstoffatomen darstellen; Y ein Halogenatom, ein Wasserstoffatom oder eine Alkoxygruppe bedeutet, und  $\gamma$  eine Zahl darstellt, die der Ungleichung  $2 \leq \gamma \leq 3$  genügt).
- 20
- 25 29. Katalysatorsystem zur  $\alpha$ -Olefin-Polymerisierung nach Anspruch 28, wobei die Organoaluminiumverbindung ein Trialkylaluminium-, ein Gemisch eines Trialkylaluminium- und eines Dialkylaluminiumhalogenids oder ein Alkylalumoxan ist.
- 30 30. Katalysatorsystem nach Anspruch 25, wobei zusätzlich ein Elektronendonator (C) zugegeben wird.
- 35 31. Katalysatorsystem nach Anspruch 30, wobei der Elektronendonator (C) eine Verbindung, ausgewählt aus Organosiliciumverbindungen mit einer Si-OR<sup>2</sup>-Bindung ( $R^2$  bedeutet einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen) oder einer Si-N-C-Bindung, aromatischen Carbonsäureesterverbindungen und sterisch gehinderten Aminen, ist.
- 40 32. Katalysatorsystem nach Anspruch 31, wobei der Elektronendonator eine Organosiliciumverbindung ist.
- 45 33. Katalysatorsystem nach Anspruch 32, wobei die Organosiliciumverbindung eine Alkoxysilanverbindung, wiedergegeben durch die allgemeine Formel  $R^{14}_tSi(OR^2)_{4-t}$  ist (wobei  $R^{14}$  und  $R^2$  jeweils einen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen bedeutet und t eine Zahl bedeutet, die der Ungleichung  $0 \leq t \leq 3$  genügt).
- 50 34. Katalysatorsystem nach Anspruch 30, wobei der Elektronendonator in einer Menge von 0,01 bis 5 Mol pro Mol Aluminiumatom in der Organoaluminiumverbindung (B) verwendet wird.
- 55 35. Verfahren zur Herstellung eines thermoplastischen Elastomergranulats und eines Elastomergranulats, umfassend das Polymerisieren eines  $\alpha$ -Olefins oder Copolymerisieren von  $\alpha$ -Olefinen, unter Verwendung eines Katalysatorsystems nach Anspruch 25, umfassend zumindest einen festen Katalysatorbestandteil (A), enthaltend als Katalysatorbestandteile mindestens Titan, Magnesium und Chlor, die in einen organischen porösen Polymerträger imprägniert sind, der einen durchschnittlichen Teilchendurchmesser von 5 bis 1000  $\mu m$  und ein Porenvolumen von 0,1 ml/g oder darüber bei einem Porenradius von 100 bis  $5000 \cdot 10^{-10}$  m (100 bis 5000 Å) aufweist, und eine Organoaluminiumverbindung (B).
36. Verfahren nach Anspruch 35, wobei das Verfahren einen ersten Schritt, der Herstellung eines isotaktischen Polypropylens durch Polymerisieren in verflüssigtem Propylen und/oder in der Gasphase umfaßt,



gefolgt von einem zweiten Schritt, der Herstellung eines statistischen Ethylen- $\alpha$ -Olefinocopolymers in der Gasphase, so daß ein Ethylengehalt in dem Copolymer im zweiten Schritt erzeugt wird, der 5 bis 95 Gew.-% erreicht, und dessen Staudinger-Index in Tetralin bei 135°C 0,3 bis 10 annimmt und das Gewicht des im zweiten Schritt hergestellten Copolymers 60 bis 97 Gew.-%, bezogen auf das Gesamtgewicht des Polymers, ausmacht.

37. Verfahren nach Anspruch 35, wobei das Verfahren einen ersten Schritt, der Polymerisierung von Ethylen im aufgeschlammten Zustand in einem Propanlösungsmittel oder einem Butanlösungsmittel oder Polymerisieren von Ethylen in der Gasphase umfaßt, gefolgt von einem zweiten Schritt, der Herstellung eines statistischen Ethylen- $\alpha$ -olefinocopolymers durch Polymerisierung in der Gasphase, so daß der Ethylengehalt in dem hergestellten Copolymer im zweiten Schritt 5 bis 95 Gew.-% erreicht und dessen Staudinger-Index in Tetralin bei 135°C 0,3 bis 10 ausmacht und das Gewicht des im zweiten Schritt hergestellten Copolymers 60 bis 97 Gew.-%, bezogen auf das Gesamtgewicht des Polymers, ausmacht.

38. Verfahren nach Anspruch 35, wobei das Verfahren die Durchführung einer statistischen Copolymerisation von Ethylen und  $\alpha$ -Olefin in der Gasphase umfaßt, so daß der Ethylengehalt in dem so hergestellten Copolymer 5 bis 95 Gew.-% erreicht und dessen Staudinger-Index in Tetralin bei 135°C 0,3 bis 10 annimmt.

39. Verfahren nach Anspruch 35, wobei das Katalysatorsystem zusätzlich einen Elektronendonator (C) enthält.

#### Revendications

1. Composant de catalyseur solide pour la polymerisation d' $\alpha$ -oléfines, contenant comme composants de catalyseur au moins du titane, du magnésium et du chlore, qui ont été imprégnés dans un support polymère poreux organique ayant un diamètre moyen de particules de 5 à 1 000  $\mu\text{m}$  et un volume de pore de 0,1 ml/g ou plus pour un rayon de pore de 100 à 5 000  $\cdot 10^{-10}$  m (100 à 5 000 Å).
2. Composant de catalyseur solide selon la revendication 1, dans lequel les rapports atomiques titane/magnésium et chlore/magnésium sont respectivement de 0,01-0,8 et 1,8-10.
3. Composant de catalyseur solide selon la revendication 1, dans lequel la quantité de composant catalytique imprégné dans le support polymère poreux organique est de 1 à 70% en poids dans le composant de catalyseur solide.
4. Composant de catalyseur solide selon la revendication 1, dans lequel le support polymère poreux organique est constitué par des billes poreuses de polymère choisi dans le groupe comprenant les polystyrènes, les poly(chlorures de vinyle), les polyoléfines et les polyacrylonitriles.
5. Composant de catalyseur solide selon la revendication 1, qui est un composant de catalyseur solide contenant un composé du titane trivalent obtenu en réduisant un composé du titane représenté par la formule générale  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (dans laquelle  $\text{R}^1$  est un groupement hydrocarboné de 1 à 20 atomes de carbone, X est un atome d'halogène; et n est un nombre satisfaisant la relation  $0 < n \leq 4$ ) avec un composé organomagnésien en présence d'un support polymère poreux organique ayant un diamètre moyen de particules de 5 à 1000  $\mu\text{m}$  et un volume de pore de 0,1 ml/g ou plus pour un rayon de pore de 100 à 5 000  $\cdot 10^{-10}$  m (100 à 5 000 Å); ou en la présence simultanée dudit support polymère poreux organique et d'un composé organosilicié ayant une liaison Si-O, pour obtenir un produit solide, et en traitant le produit solide par un ester et par un mélange d'un éther et de tétrachlorure de titane.
6. Composant de catalyseur solide selon la revendication 1, qui est un composant de catalyseur solide contenant un composé du titane trivalent obtenu en réduisant un composé du titane représenté par la formule générale  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (dans laquelle  $\text{R}^1$  est un groupement hydrocarboné de 1 à 20 atomes de carbone, X est un atome d'halogène; et n est un nombre satisfaisant la relation  $0 < n \leq 4$ ) avec un composé organomagnésien en présence d'un support polymère poreux organique ayant un diamètre moyen de particules de 5 à 1000  $\mu\text{m}$  et un volume de pore de 0,1 ml/g ou plus pour un rayon de pore de 100 à 5 000  $\cdot 10^{-10}$  m (100 à 5 000 Å); ou en la présence simultanée dudit support polymère



poreux organique et d'un composé organosilicié ayant une liaison Si-O, pour obtenir un produit solide, et en traitant le produit solide par un mélange d'un éther et de tétrachlorure de titane.

7. Composant de catalyseur solide selon la revendication 5 ou 5, dans lequel le groupement hydrocarboné R<sup>1</sup> du composé de titane représenté par la formule générale  $Ti(OR^1)_nX_{4-n}$  est un groupement alkyle ayant de 2 à 18 atomes de carbone ou un groupement aryle ayant de 6 à 18 atomes de carbone.
8. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel le X du composé de titane représenté par la formule générale  $Ti(OR^1)_nX_{4-n}$  est la chlore.
9. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel n du composé de titane représenté par la formule générale  $Ti(OR^1)_nX_{4-n}$  est un nombre satisfaisant la relation  $2 \leq n \leq 4$ .
10. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel le composé organomagnésien est un composé de Grignard représenté par la formule générale  $R'Mgx$  (dans laquelle R' est un groupement hydrocarboné de 1 à 20 atomes de carbone et X est un atome d'halogène), ou un composé de dialkylmagnésium ou un composé de diarylmagnésium tous deux représentés par la formule générale  $R''R'''Mg$  (dans laquelle R'' et R''' sont chacun un groupement hydrocarboné ayant de 1 à 20 atomes de carbone).
11. Composant de catalyseur solide selon la revendication 5, dans lequel l'ester est un ester d'acide monocarboxylique ou polycarboxylique.
12. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel l'éther est un éther dialkyle.
13. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel le composé organosilicié ayant une liaison Si-O est représenté par les formules générales suivantes :
 
$$Si(OR^3)_mR^4_{4-m},$$

$$R^5(R^6_2SiO)_pSiR^7_3 \text{ ou } (R^8_2SiO)_q$$
 (dans lesquelles R<sup>3</sup> est un groupement hydrocarboné ayant de 1 à 20 atomes de carbone; R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> et R<sup>8</sup> sont chacun un groupement hydrocarboné ayant de 1 à 20 atomes de carbone ou un atome d'hydrogène; m est un nombre satisfaisant la relation  $0 < m \leq 4$ ; p est un entier de 1 à 1 000; et q est un entier de 2 à 1 000).
14. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel le composé organosilicié ayant une liaison Si-O est un alcoxyasilane représenté par la formule générale  $Si(OR^3)_mR^4_{4-m}$ , dans laquelle m est un nombre satisfaisant la relation  $1 \leq m \leq 4$ .
15. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel le composé organosilicié ayant une liaison Si-O est utilisé à raison de 1 à 50, exprimé en rapport atomique des atomes de silicium aux atomes de titane dans le composé de titane.
16. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel le composé organomagnésien est utilisé à raison de 0,1 à 10, exprimé en rapport atomique de la somme des atomes du titane et des atomes de silicium aux atomes de magnésium.
17. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel la réduction est effectuée à une température de -50 ° à +70 °C.
18. Composant de catalyseur solide selon la revendication 5, dans lequel l'ester est utilisé à raison de 0,1 à 50 moles par mole d'atomes de titane dans le produit solide.
19. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel d'éther est utilisé à raison de 0,1 à 100 moles par mole d'atomes de titane dans le produit solide.



20. Composant de catalyseur solide selon la revendication 5 ou 6, dans lequel de tétrachlorure de titane est utilisé à raison de 2 à 2 000 moles par mole d'atomes de titane dans de produit solide et à raison de 1 à 100 moles par mole d'éther.
- 5 21. Composant de catalyseur solide selon la revendication 5, dans lequel le produit solide est traité par un ester dans un diluant, à une température de  $-50^{\circ}$  à  $+150^{\circ}$  C.
22. Composant de catalyseur solide selon la revendication 21, dans lequel le diluant est un hydrocarbure aromatique ou un hydrocarbure halogéné.
- 10 23. Composant de catalyseur solide selon la revendication 5, dans lequel le produit solide traité par un ester est traité avec un mélange d'un éther et de tétrachlorure de titane à l'état de suspension, en utilisant un solvant, à une température de  $30^{\circ}$  à  $150^{\circ}$  C.
- 15 24. Composant de catalyseur solide selon la revendication 23, dans lequel le solvant est un hydrocarbure aliphatique, un hydrocarbure aromatique, un hydrocarbure alicyclique ou un hydrocarbure halogéné.
25. Système catalytique pour la polymérisation d' $\alpha$ -oléfines comprenant au moins  
 (A) un composant de catalyseur solide selon la revendication 1, contenant comme composants de catalyseur au moins du titane, du magnésium et du chlore qui ont été imprégnés dans un support polymère poreux organique ayant un diamètre moyen de particules de 5 à 1 000  $\mu\text{m}$  et un volume de pore de 0,1 ml/g ou plus pour un rayon de pore de 100 à 5 000  $\cdot 10^{-10}$  m (100 à 5 000 Å), et  
 (B) un composé organoaluminique.
- 20 26. Système catalytique selon la revendication 25, dans lequel le composant de catalyseur solide est un composant de catalyseur solide contenant un composé du titane trivalent obtenu en réduisant un composé du titane représenté par la formule générale  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (dans laquelle  $\text{R}^1$  est un groupement hydrocarboné de 1 à 20 atomes de carbone, X est un atome d'halogène; et n est un nombre satisfaisant la relation  $0 < n \leq 4$ ) avec un composé organomagnésien en présence d'un support polymère poreux organique ayant un diamètre moyen de particules de 5 à 1000  $\mu\text{m}$  et un volume de pore de 0,1 ml/g ou plus pour un rayon de pore de 100 à 5 000  $\cdot 10^{-10}$  m (100 à 5 000 Å); ou en la présence simultanée dudit support polymère poreux organique et d'un composé organosilicié ayant une liaison Si-O, pour obtenir un produit solide, et en traitent le produit solide par un ester et par un mélange d'un éther et de tétrachlorure de titane.
- 30 27. Système catalytique selon la revendication 25, dans lequel le composant de catalyseur solide est un composant de catalyseur solide contenant un composé du titane trivalent obtenu en réduisant un composé du titane représenté par la formule générale  $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$  (dans laquelle  $\text{R}^1$  est un groupement hydrocarboné de 1 à 20 atomes de carbone, X est un atome d'halogène; et n est un nombre satisfaisant la relation  $0 < n \leq 4$ ) avec un composé organomagnésien en présence d'un support polymère poreux organique ayant un diamètre moyen de particules de 5 à 1000  $\mu\text{m}$  et un volume de pore de 0,1 ml/g ou plus pour un rayon de pore de 100 à 5 000  $\cdot 10^{-10}$  m (100 à 5 000 Å); ou en la présence simultanée dudit support polymère poreux organique et d'un composé organosilicié ayant une liaison Si-O, pour obtenir un produit solide, et en traitant le produit solide par un mélange d'un éther et de tétrachlorure de titane.
- 35 28. Système catalytique pour la polymérisation d' $\alpha$ -oléfines selon la revendication 25, dans lequel le composé organoaluminique (B) est un composé ayant au moins une liaison Al-C dans le molécule et est représenté par les formules générales
- 50 
$$\text{R}^9_\gamma\text{AlY}_{3-\gamma}\text{ou}$$

$$\text{R}^{10}\text{R}^{11}\text{Al-O-AIR}^{12}\text{R}^{13}$$
- (dans lesquelles  $\text{R}^9$ ,  $\text{R}^{10}$ ,  $\text{R}^{11}$ ,  $\text{R}^{12}$  et  $\text{R}^{13}$  sont chacun un groupement hydrocarboné ayant de 1 à 8 atomes de carbone; Y est un atome d'halogène, un atome d'hydrogène ou un groupement alcoxy; et  $\gamma$  est un nombre satisfaisant la relation  $2 \leq \gamma \leq 3$ ).
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29. Système catalytique pour la polymérisation d' $\alpha$ -oléfines selon la revendication 28, dans lequel le composé organoaluminique est un trialkylaluminium, un mélange d'un trialkylaluminium et d'un halogénure de dialkylaluminium, ou un alkylalumoxane.
- 5 30. Système catalytique selon la revendication 25, dans lequel on ajoute en outre un donneur d'électrons (C).
- 10 31. Système catalytique selon la revendication 30, dans lequel le donneur d'électrons C est un composé choisi dans le groupe comprenant les composés organosiliciés ayant une liaison Si-OR<sup>2</sup> (R<sup>2</sup> représentant un reste hydrocarboné ayant de 1 à 20 atomes de carbone) ou une liaison Si-N-C, les esters carboxyliques aromatiques et les amines stériquement encombrées.
- 15 32. Système catalytique selon la revendication 31, dans lequel le donneur d'électrons est un composé organosilicié.
- 20 33. Système catalytique selon la revendication 32, dans lequel le composé organosilicié est un alcoxysilane représenté par la formule générale R<sup>14</sup><sub>t</sub>Si(OR<sup>2</sup>)<sub>4-t</sub> (dans laquelle R<sup>14</sup> et R<sup>2</sup> représentent chacun un reste hydrocarboné ayant de 1 à 20 atomes de carbone et t représente un nombre satisfaisant la relation  $0 \leq t \leq 3$ ).
- 25 34. Système catalytique selon la revendication 30, dans lequel le donneur d'électrons est utilisé à raison de 0,01 à 5 moles par mole d'atomes d'aluminium dans le composé organoaluminique (B).
- 30 35. Procédé de production d'un élastomère thermoplastique granulaire ou d'un élastomère granulaire qui consiste à polymériser une  $\alpha$ -oléfine ou à copolymériser des  $\alpha$ -oléfines par utilisation d'un système catalytique selon la revendication 25 comprenant au moins un composant de catalyseur solide (A) contenant comme composants de catalyseur au moins du titane, du magnésium et du chlore qui ont été imprégnés dans un support polymère poreux organique ayant un diamètre moyen de particules de 5 à 1 000  $\mu\text{m}$  et un volume de pore de 0,1 ml/g ou plus pour un rayon de pore de  $100 \text{ à } 5\,000 \cdot 10^{-10} \text{ m}$  (100 à 5 000 Å), et un composé organoaluminique (B).
- 35 36. Procédé selon la revendication 35, dans lequel le procédé consiste, dans la première étape, à préparer un polypropylène isotactique par une réaction de polymérisation dans du propylène liquéfié et/ou en phase gazeuse, puis, dans la seconde étape, à préparer un copolymère statistique éthylène/ $\alpha$ -oléfine en phase gazeuse de sorte que la teneur en éthylène dans le copolymère formé dans la deuxième étape atteigne 5 à 95% en poids et que sa viscosité intrinsèque dans la tétraline à 135 °C soit de 0,3 à 10 et que le poids du copolymère formé dans la seconde étape soit de 60 à 97% en poids par rapport au poids total des polymères.
- 40 37. Procédé selon la revendication 35, dans lequel le procédé consiste, dans la première étape, à polymériser de l'éthylène en suspension dans un solvant qui est le propane ou le butane ou à polymériser l'éthylène en phase gazeuse puis, dans la deuxième étape, à préparer un copolymère statistique éthylène/ $\alpha$ -oléfine par une réaction de polymérisation en phase gazeuse de sorte que la teneur en éthylène dans le copolymère formé dans la deuxième étape atteigne de 5 à 95%, en poids, sa viscosité intrinsèque dans la tétraline à 135 °C atteigne 0,3 à 10 et le poids du copolymère formé dans la seconde étape soit de 60 à 97% en poids par rapport au poids total des polymères.
- 45 38. Procédé selon la revendication 35, dans lequel le procédé consiste à effectuer une copolymérisation statistique d'éthylène et d' $\alpha$ -oléfine en phase gazeuse pour que la teneur en éthylène dans le copolymère ainsi formé atteigne 5 à 95%, en poids et sa viscosité intrinsèque dans la tétraline à 135 °C atteigne de 0,3 à 10.
- 50 39. Procédé selon la revendication 35, dans lequel le système catalytique contient en outre un donneur d'électrons (C).
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