

PATENT SPECIFICATION

(11) 1 503 779

1 503 779

- (21) Application No. 20721/75 (22) Filed 15 May 1975
(31) Convention Application No. 49/058 378
(32) Filed 25 May 1974
(31) Convention Application No. 49/066 515
(32) Filed 13 June 1974
(31) Convention Application No. 49/110 004
(32) Filed 26 Sept. 1974 in
(33) Japan (JP)
(44) Complete Specification published 15 March 1978
(51) INT CL² C08F 4/54
(52) Index at acceptance
C3P 404 438 440 446 448 452 454 464 472 474 486 500 512
548 578 GU
(72) Inventors FTSUHO AISHIMA, HISAYA SAKURAI, YUKICHI
TAKASHI, HIDEO MORITA, TADASHI
IKEGAMI and TOSHIO SATO



(54) CATALYST AND PROCESS FOR POLYMERISING ETHYLENE AND PROPYLENE

(71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, of No. 25-1, 1-chome, Dojimahamadori, Kitaku, Osaka, Japan, a Japanese body corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to catalyst for polymerization of ethylene and propylene and for copolymerization of ethylene or propylene and another olefin. More particularly, it relates to a novel process for low-pressure polymerization of ethylene by means of a catalyst derived from an organoaluminum-magnesium complex.

In connection with the process for low-pressure polymerization of ethylene in the presence of a catalyst consisting of a compound of transition metals belonging to Groups IV—VIA or the Periodic Table and an organometallic compound of metals belonging to Groups I—III of the Periodic Table, there have been developed and proposed numerous catalysts since the discovery of Ziegler's catalyst. Most of these are, however, so deficient in catalytic activity that a step is necessary for removing the catalyst from the polymer and this results in higher catalyst cost.

In recent years, extensive developments for highly active catalysts have been made with the view of omitting the catalyst removal step, simplifying the manufacturing process and reducing the catalyst cost.

The catalyst system known as high-activity catalyst is roughly classified into two groups. That is, the so-called supported catalyst resulting from the synthesis of the Ziegler catalyst on a certain solid surface; and a catalyst system prepared by combining a solid component made by reducing a titanium or vanadium compound with a specific organometallic compound, and a specific organometallic activator. It is known that many of the supported catalysts can provide much higher activity employing as support a halide, hydroxyhalide, alkoxide or organic acid salt, of magnesium (for example, Japanese Patent Publication Nos. 13050—1968, 42039—1972 and 42137—1972 and Japanese laid open Patent Application No. 5941—1972). As the catalyst system derived from a specific organometallic compound and a transition metal are known: a catalyst prepared from a solid component prepared by reacting a Grignard reagent or a compound of RMgOR^1 made in an inert medium and a transition metal compound (for example, West German laid open Application No. 2,024,558 and British Patent No. 1,299,862); a catalyst made from a solid compound prepared by reacting a specific organo-aluminum compound with a titanium compound (Japanese Patent Publication No. 26380—1972); and a catalyst prepared from a solid compound containing titanium- and vanadium compound (for example,

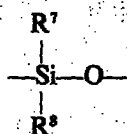
Japanese Patent Publication Nos. 28708—1972 and 28709—1972). Each of these catalysts has a satisfactory activator per unit weight of transition metal component but does not have a sufficiently high activity per unit weight of solid component. Accordingly, when the catalyst removal step is wholly omitted there will remain unsolved difficulties such as deterioration of the polymer due to halogen remaining in the polymer and corrosion of the manufacturing equipment.

We have continued intensive studies of catalysts having a high activity per unit weight of solid component and have found that an highly active catalyst is obtainable by combining the reaction product of a specific organoaluminum-complex and a titanium or vanadium compound, with an organo-aluminum compound.

According to the present invention there is provided a catalyst for the polymerization of ethylene or propylene or the copolymerization thereof with another olefin, the catalyst being prepared by forming a hydrocarbon insoluble product (A) by reacting:

either (i) a hydrocarbon-soluble organoaluminum-magnesium complex represented by the general formula $Al_nMg_sX_pY_qR^1R^2$ wherein R^1 and R^2 are each a hydrogen atom or a hydrocarbon radical having 1—10 carbon atoms; X and Y are the same or different and selected from OR^3 or $OSiR^4R^5R^6$ wherein R^3 is a hydrocarbon radical having 1—10 carbon atoms; R^4 , R^5 and R^6 are each a hydrogen atom or a hydrocarbon radical having 1—12 carbon atoms; α and β are each a number more than zero, $\beta/\alpha=1-10$, $p+q+r+s=3\alpha+2\beta$ and $0 < (p+q)/(\alpha+\beta) \leq 0.08$, or

(ii) a reaction product of a complex having the general formula of $Al_nMg_sR^1R^2$, which corresponds to $p+q=0$ in the general formula (i), with a linear or cyclic siloxane compound having a constitutional unit of



(wherein R^7 and R^8 are each a hydrogen atom or a hydrocarbon radical having 1—10 carbon atoms), with (iii) one or more titanium or vanadium compounds having at least one halogen atom, and subsequently reacting the thus obtained hydrocarbon-insoluble reaction product (A) with an organoaluminum compound (B) represented by the general formula AlR_mZ_n wherein R^9 is a hydrocarbon radical having 1—20 carbon atoms; Z is selected from a hydrogen atom, halogen atom, alkoxy group, aryloxy group and siloxy group; and m is a number in the range 2—3.

According to this invention, it is possible to attain as great an activity as 30,000 g or more of polymer per g of solid component of the catalyst, whereas, according to the patents concerning high-activity catalysts that have already been disclosed (for example, the Japanese Patents stated above), the activity obtained is below 10,000g. A catalyst made from an organomagnesium compound and a transition metal compound has already been disclosed (Japanese Patent Publication No. 1546/1957). Since organomagnesium compounds are, however, insoluble in inert hydrocarbon solvents, they cannot be used to their full effectiveness or achieve high activity. To overcome these difficulties, attempts were made to use special forms of organomagnesium compound (West German laid open patent specification No. 2,024,558, Dutch patent No. 7,103,232 and British patent No. 1,299,862). We also have found that a new catalyst is obtainable by incorporating a solid reaction product which is synthesized from a hydrocarbon-soluble organoaluminum-magnesium complex represented by the general formula $Al_nMg_mR_nR^1_{2m}$ wherein R and R^1 are a hydrogen atom or hydrocarbon radicals, n and m are numbers of each greater than zero and a titanium or vanadium compound, with an hydrocarbon-soluble organoaluminum compound. This catalyst is the subject of our patent application No. 14967/75 (Serial No. 1,498,852) and has a much higher activity than those of prior art cited above. As a result of extensive studies, we have also found to our surprise that an organoaluminum-magnesium complex having alkoxy, aryloxy, siloxy or siloxane groups is soluble in hydrocarbon solvents. We have achieved a super-active catalyst derived from this peculiar complex. In contrast, when an alkoxy or aryloxy group is introduced, in the molar range according to this invention, into a dialkyl-

magnesium compound generally represented by R_2Mg , there is formed a hydrocarbon-insoluble compound.

If said aluminum-magnesium complex containing alkoxy, aryloxy, siloxy or siloxane groups is reacted with a solid titanium or vanadium compound which is then combined with an organoaluminum compound to make the specified catalyst for polymerization of ethylene, the catalytic activity is increased with an increase in the content of alkoxy, aryloxy, siloxy or siloxane groups but decreases after passing a maximum value. It becomes easier to control the molecular weight and the resultant polymer has narrower molecular weight distribution and excellent structural regularity. The superiority of this catalyst will be described by way of Example 1 and Comparative Example 1. MI appearing therein denotes melt index and was measured at 190°C and at 2.16 kg load in accordance with ASTM, D-1238. FR represents a quotient obtained by dividing the MI value determined at 21.6 kg load by MI determined at 2.16 kg and is a measure of molecular weight distribution; the lower the value, the narrower the molecular weight distribution. As apparent from the comparison between Example 1 and Comparative Example 1, the catalyst according to the present invention also gives better results than our prior catalysts. That is, it provides polymers having higher MI, i.e. lower molecular weight, although the catalyst activity is a little lower. Therefore, in manufacturing polymers of the same molecular weight under a specified polymerization pressure, it is possible to reduce the amount of hydrogen used and raise the partial pressure of ethylene in a relative manner and thus to increase the polymerization activity. The polymer has so narrow a molecular weight distribution that a sufficiently high strength can be obtained even using low molecular weight polymers. This makes the polymer suitable for the production of large articles by injection molding methods.

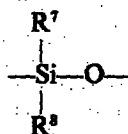
Further description will now be made of organoaluminum-magnesium complexes represented by the general formula $Al_\alpha Mg_\beta X_p Y_r R^1 R^2$, wherein R^1 , R^2 , X and Y; α and β ; p, q, r and s have all the same meanings and/or relationships as above described.

The hydrocarbon radical represented by R^1 in the above-mentioned formula, having 1 to 10 carbon atoms is preferably alkyl, for example, methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl, and the hydrocarbon radical represented by R^2 , having 1 to 10 carbon atoms may be alkyl or aryl, for example, methyl, ethyl, propyl, butyl, amyl, hexyl, octyl or phenyl are suitable radicals. As for the radicals OR^3 and $OSiR^4 R^5 R^6$ represented by X and Y, the hydrocarbon radical R^3 having 1—10 carbon atoms may be an alkyl, a cycloalkyl or an aryl radical, and is preferably a methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl, cyclohexyl or phenyl radical, R^4 , R^5 and R^6 may be a hydrogen atom or the same or different hydrocarbon radicals having 1—12 carbon atoms, and alkyl radicals such as methyl, ethyl, propyl, butyl, hexyl, octyl; cycloalkyl radicals such as cyclohexyl, methylcyclohexyl; aryl radicals such as phenyl, naphthyl are preferable. Illustrative siloxy radicals include methyldihydrosiloxy, dimethyldihydrosiloxy, trimethylsiloxy, methylethylhydrosiloxy, methyldiethylsiloxy, triethylsiloxy, methylbutylhydrosiloxy, dimethylbutylsiloxy, methylphenylhydrosiloxy, ethylphenylhydrosiloxy, methylethylphenylsiloxy, triphenylsiloxy, α -naphthylphenylmethylsiloxy. The ratio of magnesium to aluminum β/α is particularly important in preparing the active solid component of the present invention. In order to synthesize a suitably active solid component, it is important that the complex used in the synthesis takes part in the synthesis reaction effectively under the reaction condition. For that purpose, the existence of aluminum component suitable to solubilize the complex is important. Too high a value of β/α and too low a value reduce solubility of the complex. If β/α is low, the proportion of aluminum component becomes larger, resulting in reduction of catalyst activity. As evident from Examples 10—13 and Comparative Example 3 hereinafter described, the effective range of β/α is 1—10 and the preferable range is 2—6. The content of X and Y radical, $(p+q)/(\alpha+\beta)$ is also important in attaining the effectiveness of the present invention. As evident from Examples 2—4 and Comparative Example 2 hereinafter described, for high values of $(p+q)/(\alpha+\beta)$, catalyst activity is reduced. Accordingly, the upper limit is set at $(p+q)/(\alpha+\beta) \leq 0.8$. In order to obtain a polymer having a narrow molecular weight distribution, $(p+q)/(\alpha+\beta)$ is preferably in the range of 0.30—0.80. The siloxy-radical-containing complex is preferable because even if its content is increased, reduction of activity is less compared with the complex containing alkoxy or aryloxy radicals. The organoaluminum-magnesium complex can be made by: (1) reacting an organoaluminum compound

(12) (13)

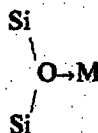
represented by the general formula AlR'_3 (R' is as defined above) and an organomagnesium compound represented by the general formula MgR^2_2 or R^2MgQ (R^2 is as defined above and Q is a halogen), and subsequently reacting the resultant hydrocarbon-soluble complex [Deutsches Patentamt Auslegeschrift 2,232,685 and Annalen des Chemie 605, 63 (1957)] and oxygen or an alcohol, silanol, aldehyde, ketone or ester of carboxylic acid; or (2) reacting an organomagnesium compound represented by R^2_2Mg with an alkoxy, aryloxy or siloxy aluminum; or (3) reacting alkoxy, aryloxy or siloxy magnesium represented by $R^2Mg(X)$ with AlR'_3 .

The siloxane compounds having the general formula of



will now be described in more detail. The substituents R^7 and R^8 are a hydrogen atom or the same or different hydrocarbon radicals having 1—10 carbon atoms. Among the hydrocarbon radicals, methyl, ethyl, propyl, butyl, hexyl, octyl, cyclohexyl, phenyl are preferred. These compounds can be used in the form of linear or cyclic dimeric or polymeric (i.e. greater than dimeric) compounds consisting of one or more kinds of the constitutional unit. Illustrative compounds include symmetric dihydrotetramethyldisiloxane, hexamethyldisiloxane, pentamethyltrihydrotetrasiloxane, cyclic methylhydrotetrasiloxane, polymethylhydrosiloxane (terminally blocked with methyl group), polydimethylsiloxane, polyphenylhydrosiloxane (terminally blocked with methyl group), and polymethylphenylsiloxane.

The reaction of organoaluminum-magnesium complex and siloxane may be carried out in an inert reaction medium (e.g. hexane, heptane, benzene or toluene) at a temperature of -20 to $150^\circ C$ with a reaction ratio of $(Si-O)/(Mg+Al)$ in the range of $0.3-5$, preferably $0.5-2$. In this reaction, the formation of the linkage $Si-O-M$ and the coordination linkage



(wherein M is Al or Mg) is confirmed by infrared spectrum analysis and nuclear magnetic resonance spectrum analysis. It is preferable that the mole ratio of $(Si-O-M)/(Al+Mg)$ in the complex is 0.8 or less, in the point of activity. The above-mentioned coordination linkage is preferable because it does not affect the activity, narrows the molecular weight distribution and at the same time lowers the chlorine content of the solid component $[Al]$.

The structure of the complex (i) is not known, but, it is assumed that there results a single or multiple complex consisting of aluminum and magnesium components. This assumption is based on the fact that the reaction product made from R^2_2Mg and oxygen or alcohol is insoluble in inert hydrocarbon solvents whereas complex (i) is soluble in those media when X and Y are OR^3 . It is also presumed that there occurs an exchange reaction between hydrocarbon alkoxy or aryloxy radicals connected respectively with aluminum and magnesium.

The titanium or vanadium compound having at least one halogen atom [catalyst component (iii)] includes titanium and vanadium halides, hydroxy halides and alkoxy halides, for example titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, ethoxytitanium trichloride, propoxytitanium trichloride, butoxytitanium trichloride, dibutoxytitanium dichloride, tributoxytitanium monochloride, vanadium tetrachloride, vanadyl trichloride, monobutoxyvanadyl dichloride, dibutoxyvanadyl monochloride. Those compounds containing three or more halogen atoms are preferred.

The reaction conditions between the organoaluminum-magnesium complex and the titanium or vanadium compound are extremely important for attaining an effective catalyst and the reaction is typically effected at a temperature up to $100^\circ C$, preferably below $20^\circ C$ in an inert reaction medium, e.g. aliphatic hydrocarbon such as hexane or heptane; aromatic hydrocarbon such as benzene, toluene or xylene; or alicyclic hydrocarbon such as cyclohexane or

13
14

methylcyclohexane. In order to achieve high catalyst activity it is recommended that the reaction ratio is 0.05—50 mols, especially 0.2—5 mols, of the organo-aluminum-magnesium complex per mol of the titanium or vanadium compound. The number of moles for said organoaluminum-magnesium complex means the molar sum of aluminum and magnesium components. Taking as an example $\text{AlMg}_2(\text{O}-\text{nC}_4\text{H}_9)_{2.5} (\text{C}_2\text{H}_5)_{2.5} (\text{n}-\text{C}_4\text{H}_9)_6$, 722.3 grams (corresponding to the molecular weight of the above structural formula) is equivalent to 5 mols. In order to attain high catalyst activity, the simultaneous addition process in which two catalyst components are introduced simultaneously into a reaction zone is especially suitable. The hydrocarbon-insoluble reaction product may be used directly, provided the reaction is complete. It is desirable, however, to isolate it from the reaction mixture to enhance the reproducibility of polymerization.

By further reaction of the hydrocarbon-insoluble reaction product thus obtained, with a halide of aluminum, silicon, tin, titanium or vanadium, a catalyst promoting the production of a polymer having a more uniform particle size and high bulk density can be synthesized.

As the organoaluminum compound (catalyst component B) there is used one or more compounds denoted by the general formula $\text{AlR}_m^{\text{R}^1}\text{Z}$. R^1 is a hydrocarbon radical containing 1—20 carbon atoms and may be an aliphatic, aromatic or alicyclic hydrocarbon radical. The radical denoted by Z is a hydrogen atom, halogen atom, alkoxy radical, aryloxy radical or siloxy radical and m is 2 or 3. Recommended compounds include, for example, triethylaluminum, tri-*n*-propylaluminum, tri-isopropylaluminum, tri-*n*-butylaluminum, tri-isobutylaluminum, tri-hexylaluminum, tri-octylaluminum, tri-decylaluminum, tri-dodecylaluminum, tri-hexadecylaluminum, diethylaluminum hydride, di-isobutylaluminum hydride, diethylaluminum ethoxide, di-isobutylaluminum ethoxide, di-octylaluminum butoxide, di-isobutylaluminum octyloxide, diethylaluminum chloride, di-isobutylaluminum chloride, dimethylhydrosiloxyaluminum dimethyl, ethylmethylhydrosiloxyaluminum diethyl, ethyldimethylsiloxyaluminum diethyl, and combinations thereof.

Employing, in combination, the above alkylaluminum compound (B) and the aforesaid hydrocarbon-insoluble solid (A) results in a highly active catalyst. To obtain an extremely highly catalytic activity, it is preferable to use especially a trialkylaluminum or dialkylaluminum hydride. When incorporating a radical Z which is electronegative to for example trialkylaluminum or dialkylaluminum hydride, the resultant catalyst tends to decrease in activity but has a characteristic polymerization behavior. As an example, introducing an alkoxy group affords easier control of molecular weight. The reaction between catalyst components (A) and (B) in accordance with the invention may be conducted by adding said both components to the polymerization system and under the polymerization conditions, or before polymerization is initiated. The reaction ratio of the components is preferably 1—3,000 m mols of component (B) per gram of component (A).

As the polymerization method there are available the usual suspension-, solution- and gas phase polymerizations. In cases of suspension or solution polymerization processes, the catalyst is let into the reactor with a polymerization medium, e.g. aliphatic hydrocarbon such as hexane or heptane; aromatic hydrocarbon such as benzene, toluene or xylene; or alicyclic hydrocarbon such as cyclohexane or methylcyclohexane. Then, ethylene is added up to 1—50 kg/cm² in an inert atmosphere and allowed to polymerize at room temperature to 150°C. On the other hand, in the case of gas phase polymerization, it is possible to carry out the polymerization under the condition of 1—50 kg/cm² pressure of ethylene at a temperature from room temperature to 120°C by using a procedure such as fluidized bed, moving bed or mixing with a stirrer in order to give better contact of ethylene with the catalyst. The catalyst can be added as it is, in the form of solution or dispersion in hydrocarbon mentioned above. In order to control the molecular weight of polymer, it is also possible to add hydrogen, a hydrocarbon halide or an organometallic compound which is liable to bring about chain transfer.

The catalyst according to this invention enables copolymerization ethylene and propylene with mono-olefins such as propylene, butene-1 or hexene-1, as well as homo polymerization of ethylene and propylene with high efficiency.

The following Examples illustrate but do not limit the invention. In the Examples, the symbols MI and FR have the meanings already mentioned above, and the units of "catalyst efficiency" are gram(s) of polymer per gram of solid component per hour per kg/cm² of ethylene pressure.

Example 1.

(1) Synthesis of the organoaluminum-magnesium complex

In a 500 ml flask, were placed 13.80 g of di-n-butylmagnesium and 2.85 g of triethylaluminum together with 200 ml of n-heptane. The mixture was reacted, with stirring, at 80°C for 2 hours. Thus a complex having the composition corresponding to $\text{AlMg}_4(\text{C}_2\text{H}_5)_3(\text{n-C}_4\text{H}_9)_8$ was synthesized. This solution was cooled down to 10°C and 50 ml of a solution of 50 m mols n-octanol in n-heptane was added, with cooling gradually, dropwise for one hour. Thus a further organo-aluminum-magnesium complex was synthesized. One portion of this solution was separated and oxidized by dry air, then hydrolyzed to convert the alkyl and alkoxy groups into their alcohols. The final product was analyzed by the gas chromatography. From the analytical values based on ethanol, n-butanol and n-octanol, the composition of the final complex proved to be $\text{AlMg}_4(\text{O-nC}_8\text{H}_{17})_{2.02}(\text{C}_2\text{H}_5)_{2.70}(\text{n-C}_4\text{H}_9)_{6.28}$.

(2) Synthesis of hydrocarbon-insoluble solid component

Oxygen and moisture inside a 500 ml flask equipped with 2 dropping funnels were removed by purging with dry nitrogen, 160 ml of n-heptane was added thereto and cooled to -20°C. Then 80 ml of n-heptane solution containing 40 m mol of the complex of the above-mentioned formula and 80 ml of n-heptane solution containing 40 m mol of titanium tetrachloride were separately introduced in the dropping funnels. Both the components were simultaneously added with stirring at -20°C for 2 hours and further reacted at this temperature for three hours. The resulting hydrocarbon-insoluble solid was isolated, washed with n-heptane and dried to give 10.8 g of the solid product.

(3) Polymerization reaction

In a 5 liter autoclave which had been evacuated and nitrogen-purged were placed 5 mg of the hydrocarbon-insoluble reaction product made in step (2) and 3.0 m mol of tri-isobutylaluminum plus 3 liter of n-heptane previously dehydrated and degassed. While the inner temperature of the autoclave was kept at 85°C, there was added hydrogen up to 3.0 kg/cm² gauge pressure followed by ethylene up to 10.0 kg/cm² total gauge pressure. With this condition the polymerization was performed for an hour. There was obtained 1.02 kg of polymer; MI, 2.76 and FR, 31. The catalyst efficiency was 29,000.

Comparative Example 1.

The synthesis of catalyst and the polymerization were conducted just as in Example 1 except that organo-aluminum-magnesium complex of the composition $\text{AlMg}_4(\text{C}_2\text{H}_5)_3(\text{n-C}_4\text{H}_9)_8$ made in Example 1 was used directly to prepare the hydrocarbon-insoluble reaction product. There was obtained 1.25 kg of polymer; MI, 0.85 and FR, 46. The catalyst efficiency was 35,700.

Example 2-4, Comparative Example 2.

A hydrocarbon-insoluble solid was synthesized similarly as in Example 1 except that organo-aluminum-magnesium complexes indicated in Table 1 were used. Polymerization was carried out under the same conditions as Example 1 by using 5 mg of the hydrocarbon-insoluble solids and 3.0 m mol of triisobutylaluminum.

TABLE 1

Examples	Organoaluminum-magnesium complex	Polymerization result			
		Yield kg	Catalyst efficiency	MI	FR
2	$\text{AlMg}_4(\text{OC}_2\text{H}_5)_{1.7}(\text{C}_2\text{H}_5)_{2.185}(\text{n-C}_4\text{H}_9)_{7.655}$	1.32	37,600	1.25	37
3	$\text{AlMg}_4(\text{OC}_2\text{H}_5)_{1.5}(\text{C}_2\text{H}_5)_{2.775}(\text{n-C}_4\text{H}_9)_{6.975}$	0.935	26,700	2.95	29
4	$\text{AlMg}_4(\text{OC}_2\text{H}_5)_{1.38}(\text{C}_2\text{H}_5)_{2.50}(\text{n-C}_4\text{H}_9)_{4.65}$	0.686	19,600	5.43	27
Comparative Example 2	$\text{AlMg}_4(\text{OC}_2\text{H}_5)_{1.05}(\text{C}_2\text{H}_5)_{1.95}(\text{n-C}_4\text{H}_9)_{4.00}$	0.189	5,200	7.20	26

Example 5.

In the same manner as in Example 1, an organo-aluminum-magnesium complex of the composition $\text{AlMg}_4(\text{O}-i\text{C}_4\text{H}_9)_{1.55}(\text{C}_2\text{H}_5)_{2.66}(\text{n-C}_4\text{H}_9)_{7.85}$ was prepared by the use of triethylaluminum, di-n-butylmagnesium and isobutanol. Then, 40 m mol of titanium tetrachloride and 80 m mol of the above complex were reacted at 0°C for 3 hours. Using 5 mg of the resultant hydrocarbon-insoluble solid and 6.0 m mol of trihexylaluminum, the polymerization was conducted as in Example 1. There was obtained 0.98 kg of polymer; MI, 3.50 and FR, 30. The catalyst efficiency was 27,900.

Example 6.

In the same way as in Example 1, organo-aluminum-magnesium complex of the composition

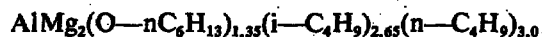


was prepared by the use of triethylaluminum, di-n-butylmagnesium and n-propanol. Then 40 m mol of titanium tetrachloride and 32 m mol of the complex were reacted at 10°C for 4 hours. Using 5 mg of the resultant hydrocarbon-insoluble solid and 6.0 m mol of trioctylaluminum, the polymerization was carried out as in Example 1. There was obtained 0.95 kg of polymer; MI, 1.65 and FR, 35. The catalyst efficiency was 27,100.

116 (17)

Example 7.

In the same manner as in Example 1, organo-aluminum-magnesium complex of the composition



5 was prepared by the use of triisobutylaluminum, di-n-butylmagnesium and n-
hexylalcohol. Then, 40 m mol of a 1:1 by mole mixture of titanium tetrachloride
and monobutoxytitanium trichloride and 40 m mol of the above complex were
10 reacted at 0°C for 4 hours. Using 5 mg of the resultant hydrocarbon-insoluble solid
and 3.0 m mol of triisobutylaluminum, the polymerization was carried out as in
Example 1. There was obtained 0.65 kg of polymer; MI, 3.60 and FR, 32. The
catalyst efficiency was 18,600. 10

Example 8.

In the same way as in Example 1, organo-aluminum-magnesium complex of the composition



15 was made by the use of tri-n-propylaluminum, di-n-hexylmagnesium and ethanol.
Then, 40 m mol of vanadium tetrachloride and 40 m mol of this complex were
reacted at -10°C for 3 hours to form a hydrocarbon insoluble solid. In a 5-liter
autoclave which had been evacuated to vacuum and then nitrogen-purged were
20 placed 5 mg of the hydrocarbon-insoluble solid and 3.0 m mol of tri-isobutyl-
aluminum together with 3 liter of n-heptane previously dehydrated and degassed.
While the inner temperature of the autoclave was kept at 85°C, there was added
hydrogen up to 2.0 kg/cm² gauge pressure followed by ethylene up to 6.0 kg/cm²
25 total gauge pressure. The polymerization was conducted for one hour while
additional ethylene was added to maintain the total gauge pressure at 6.0 kg/cm².
There was obtained 0.42 kg of polymer; MI, 1.89 and FR, 34. The catalyst
efficiency was 21,000. 25

Example 9.

30 In the same way as in Example 1, organo-aluminum-magnesium complex of
the composition $\text{AlMg}_3(\text{O}-\text{nC}_4\text{H}_9)_{3.0}(\text{n}-\text{C}_4\text{H}_9)_{10}$ was prepared by reacting 2.46 g
of tri-n-butoxyaluminum and 6.90 g of di-n-butylmagnesium at 80°C for 3 hours.
Then, 40 m mol of this complex and 40 m mol of vanadyl trichloride were reacted
at -20°C for 4 hours. Using as catalyst component 5 mg of the resultant
35 hydrocarbon-insoluble solid and 3.0 m mol of tri-decylaluminum, the
polymerization was performed as in Example 5. There was obtained 0.46 kg of
polymer; MI, 2.15 and FR, 33. The catalyst efficiency was 23,000. 35

Examples 10—14 and Comparative Example 3.

40 A hydrocarbon-insoluble solid was obtained as in Example 1 by reacting the
organoaluminum-magnesium complex indicated in Table 2 at -30°C for 4 hours.
By using 5 mg of this solid and 3 m mol of trioctylaluminum, polymerization was
carried out as in Example 8, whereby the result shown in the table was obtained. 40

TABLE 2

Examples	Organoaluminum-magnesium complex	Polymerization result			
		Yield kg	Catalyst efficiency	MI	FR
10	$\text{AlMg}_3(\text{OnC}_4\text{H}_9)_{4.53}(\text{C}_2\text{H}_5)_{2.56}(\text{n-C}_4\text{H}_9)_{11.82}$	0.374	18,700	3.13	28
11	$\text{AlMg}_6(\text{OnC}_4\text{H}_9)_{3.46}(\text{C}_2\text{H}_5)_{2.72}(\text{n-C}_4\text{H}_9)_{8.82}$	0.530	26,500	3.52	28
12	$\text{AlMg}_2(\text{OnC}_4\text{H}_9)_{1.52}(\text{C}_2\text{H}_5)_{2.80}(\text{n-C}_4\text{H}_9)_{2.68}$	0.450	22,500	2.87	29
13	$\text{AlMg}(\text{OnC}_4\text{H}_9)_{1.05}(\text{C}_2\text{H}_5)_{2.75}(\text{n-C}_4\text{H}_9)_{1.20}$	0.352	17,600	4.05	32
14	$\text{AlMg}_4(\text{OnC}_4\text{H}_9)_{2.05}(\text{C}_2\text{H}_5)_{2.02}(\text{C}_{10}\text{H}_{13})_{6.93}$	0.390	18,500	2.52	32
Comparative example 3	$\text{Al}_2\text{Mg}(\text{OnC}_4\text{H}_9)_{1.32}(\text{C}_2\text{H}_5)_{5.66}(\text{n-C}_4\text{H}_9)_{1.02}$	0.150	7,500	3.44	35

Example 15.

Using 5 mg of the hydrocarbon-insoluble solid component made in Example 1 and 6.0 m mol of organo-aluminum component of the composition $\text{Al}(\text{i-C}_4\text{H}_9)_{2.50}\text{Cl}_{0.50}$ the polymerization was carried out as in Example 1. The polymer weighed 0.92 kg; MI, 5.20 and FR, 30. The catalyst efficiency was 26,300.

5

Example 16.

Using 5 mg of the hydrocarbon-insoluble made in Example 1 and 6.0 m mol of organo-aluminum component of the composition $\text{Al}(\text{i-C}_4\text{H}_9)_{2.50}\text{Cl}_{0.50}$ the polymerization was carried out as in Example 1. The polymer weighed 0.84 kg; MI, 3.80 and FR, 31. The catalyst efficiency was 24,000.

10

Example 17.

In the same way as in Example 9, organo-aluminum-magnesium complex of the composition

15



was synthesized from diethylaluminum ethoxide and di-n-butylmagnesium. 40 m mol of titanium tetrachloride and 40 m mol of this complex were reacted at -5°C for 4 hours. The polymerization was carried out as in Example 1 except that 5 mg of the resultant hydrocarbon-insoluble solid and 3.0 m mols of triisobutylaluminum were used together with an ethylene-propylene mixture containing 3% of propylene instead of ethylene. The polymer weighed 1.26 kg; MI, 7.50 and FR, 26. The catalyst efficiency was 36,000.

20

12

18 19

Example 18.

The polymerization was performed as in Example 17 except that an ethylene-butene-1 mixture gas containing 2% of butene-1 was used instead of an ethylene-propylene mixture gas. The polymer weighed 1.08 kg; MI, 9.75 and FR, 27. The catalyst efficiency was 30,500.

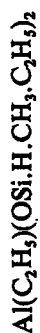
Example 19—26.

A hydrocarbon-insoluble solid was synthesized as in Example 1 by reacting (A) organoaluminum-magnesium complexes which are shown in Table 3 and obtained by reacting dialkylmagnesium and siloxaluminum compound as in Example 1, with (B) titanium tetrachloride with a mol ratio of A:B of 1:1. For the synthesis of the hydrocarbon-insoluble solid, in Examples 19—24, addition of the two components was carried out at -10°C for 2 hours and a further reaction was carried out at 5°C for 2 hours, and in Examples 25—26, addition of the two compounds was carried out at -20°C for 2 hours and a further reaction was carried out at 10°C for 2 hours. By using 5 mg of this solid and organoaluminum compound shown in Table 3, polymerization was carried out similarly as in Example 8 whereby results shown were obtained. The organoaluminum-magnesium complex in Example 26 was synthesized by the reaction of $\text{AlMg}_3(\text{C}_2\text{H}_5)_3(\text{n}-\text{C}_4\text{H}_9)_6$ and trimethylsilanol.

TABLE 3

Example	Organoaluminum-magnesium complex	Organoaluminum compound (amount used in mol)	Polymerization result			
			Yield g	MI	FR	Catalyst efficiency
19	$\text{AlMg}_2(\text{n}-\text{C}_4\text{H}_9)_2(\text{n}-\text{C}_3\text{H}_7)_4[\text{OSi}(\text{CH}_3)_2\text{n}-\text{C}_4\text{H}_9]$	$\text{Al}(\text{i}-\text{C}_4\text{H}_9)_3$ (1.5)	485	2.30	33	24,300
20	$\text{AlMg}_2(\text{C}_2\text{H}_5)_2(\text{n}-\text{C}_4\text{H}_9)_2(\text{OSi}(\text{H})\text{CH}_3)_2$	$\text{Al}(\text{C}_2\text{H}_5)_{2.5}(\text{OC}_2\text{H}_5)_{0.5}$ (3.0)	560	4.21	31	28,000
21	$\text{AlMg}_3(\text{C}_2\text{H}_5)_6(\text{OSi}(\text{H})\text{CH}_3)_2$	$\text{Al}(\text{i}-\text{C}_4\text{H}_9)_{2.5}\text{Cl}_{0.5}$ (3.0)	515	3.96	29	25,800
22	$\text{AlMg}_2(\text{C}_2\text{H}_5)_2(\text{n}-\text{C}_3\text{H}_7)_4(\text{OSi}(\text{H})\text{C}_2\text{H}_5)_2$	$\text{Al}(\text{n}-\text{C}_6\text{H}_{13})_3$ (3.0)	460	3.06	34	23,000
23	$\text{AlMg}_2(\text{C}_2\text{H}_5)_4(\text{n}-\text{C}_3\text{H}_7)_2(\text{OSi}(\text{H})\text{CH}_3)_2$	$\text{Al}(\text{n}-\text{C}_{12}\text{H}_{25})_3$ (3.0)	490	1.96	33	24,500
24	$\text{AlMg}(\text{i}-\text{C}_4\text{H}_9)_2(\text{n}-\text{C}_6\text{H}_{13})_2(\text{OSi}(\text{H})\text{CH}_3)_2$	$\text{Al}(\text{n}-\text{C}_8\text{H}_{17})_3$ (3.0)	385	4.51	30	19,300
25	$\text{AlMg}_3(\text{C}_2\text{H}_5)_{1.5}(\text{n}-\text{C}_4\text{H}_9)_{6.0}(\text{OSi}(\text{H})\text{CH}_3)_2$	$\text{Al}(\text{i}-\text{C}_4\text{H}_9)_3$ (1.5)	530	3.25	32	26,500
26	$\text{AlMg}_3(\text{C}_2\text{H}_5)_{1.55}(\text{n}-\text{C}_4\text{H}_9)_{4.25}[\text{OSi}(\text{CH}_3)_3]_{1.5}$	$\text{Al}(\text{i}-\text{C}_4\text{H}_9)_{2.5}\text{Cl}_{0.5}$ (3.0)	464	5.28	28	23,200

Di-n-butylmagnesium and a siloxyaluminum of the composition



- 5 were reacted as in Example 1 to prepare its organo-aluminum-magnesium complex. This complex and the titanium or vanadium compound shown in Table 2 were reacted in the same way under the corresponding condition shown in the Table. Utilizing 5 mg of the resultant hydrocarbon-insoluble solid and the aluminum compound shown; the polymerization was conducted under the same condition as in Example 1. The results are also given in that Table.

TABLE 4

Example	Hydrocarbon-insoluble solid			Organoaluminum compound (Amount used m mol)	Polymerization result			
	Titanium, vanadium, compound	mol ratio Al+Mg/ Ti or V	temp. x time (°C) (hr)		Yield g	MI	FR	Catalyst efficiency
27	A 2:1 mixture of TiCl_4 and TiCl_3 ($\text{O}-\pi\text{C}_4\text{H}_9$)	1/1	0x4	$\text{Al}(\text{n}-\text{C}_4\text{H}_9)_3$ (1.5)	345	5.20	28	17,300
28	VCl_4	1/1	-20x4	$\text{Al}(\text{n}-\text{C}_4\text{H}_9)_3$ (1.5)	585	2.21	36	29,300
29	A 2:1 mixture of TiCl_4 and VOCl_3	1/1	-5x4	$\text{Al}(\text{i}-\text{C}_3\text{H}_7)_3$ (1.5)	520	3.45	31	26,000
30	TiCl_4	2/1	-30x4	$\text{Al}(\text{i}-\text{C}_4\text{H}_9)_2\text{H}$ (1.5)	565	2.90	32	28,300
31	TiCl_4	0.7/1	-10x4	$\text{Al}(\text{C}_2\text{H}_5)_2\text{H}$ (1.5)	510	3.25	30	25,500

19
20

21

12

1,503,779

12

Examples 32—37.

(1) Reaction of organoaluminum-magnesium complex and siloxane

Fifty ml heptane solution containing the organoaluminum magnesium complex, synthesized as in Example 1 in a concentration of 1.0 mol/l was reacted in a 200 ml flask with 50 ml heptane solution containing a siloxane compound in a concentration of 0.5—2.0 mol/l based upon Si—O.

With regard to the organoaluminum-magnesium complex, the siloxane and the reaction conditions, those indicated in Table 5 are used.

The measurement of the Si—O—M linkage (wherein M is aluminum or magnesium) was carried out by concentrating the above-mentioned reaction product and determining the amount of gas generated at the time of decomposition with water.

(2) Synthesis of hydrocarbon-insoluble solid

By using the same method as Example 1 and under the conditions of Table 5, the synthesis of a hydrocarbon-insoluble solid was carried out.

(3) Polymerization

Five mg of the hydrocarbon-insoluble solid synthesized in (2) and various aluminum compounds were introduced in a 1.5 l autoclave which had been evacuated to vacuum and purged with nitrogen, together with dehydrated, degassed hexane. While the inside temperature of the autoclave was maintained at 85°C the pressure of hydrogen and ethylene were raised to the values indicated in Table 5 so that with the hexane vapour pressure the total pressure was 4.7 kg/cm² gauge. Polymerization was carried out for one hour while holding the total pressure at 4.7 kg/cm² gauge by feeding ethylene, whereby the result shown in Table 5 was obtained.

TABLE 5

Catalyst											
Hydrocarbon-insoluble solid											
Example	Organoaluminum-magnesium complex siloxane reaction product						Ti or V compound	Ti/Al+Mg (mol ratio)	Temp x time (hrs)	Composition % by weight	
	Organoaluminum-magnesium complex	Siloxane	Si-O/Al+Mg	temp. x time	Si-O-M /Al+Mg	Ti				Cl	
32	$\text{AlMg}_6(\text{C}_2\text{H}_5)_3(\text{n-C}_4\text{H}_9)_{12}$	Sym. tetramethyl dihydrodisiloxane	1.0	Hr 0°Cx1/2	0.17		TiCl_4	1/1	5°Cx4	13.2	37.5
33	$\text{AlMg}_2(\text{i-C}_4\text{H}_9)_3(\text{n-C}_4\text{H}_9)_4$	Methylhydro polysiloxane viscosity 30 Centistokes 30°C	1.0	Hr 100°Cx5	0.78		TiCl_4	1/1	5°Cx4	12.5	38.9
34	$\text{AlMg}_2(\text{C}_2\text{H}_5)_3(\text{n-C}_3\text{H}_7)_6$	Methylpoly-siloxane viscosity 50 Centistokes 30°C	0.8	Hr 100°Cx10	0.25		TiCl_4	2/1	10°Cx4	14.1	37.2
35	$\text{AlMg}_6(\text{C}_2\text{H}_5)_3(\text{n-C}_4\text{H}_9)_{12}$	Cyclic methylhydroxytetra siloxane	1.0	Hr 80°Cx5	0.72		TiCl_4	1/1	5°Cx4	11.2	39.2
36	ditto	ditto	ditto	ditto	0.72		VCl_4	1/1	0°Cx4	12.5	43.1
37	$\text{AlMg}_6(\text{C}_2\text{H}_5)_3(\text{n-C}_4\text{H}_9)_{12}$	Sym. tetramethyl dihydrodisiloxane	1.0	Hr 0°Cx1/2	0.17		TiCl_4	1/1	5°Cx4	13.2	37.5

22 23

1,503,779

14

TABLE 5 (Continued)

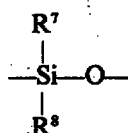
Catalyst Organoaluminum compounds (amount used m mol)	Polymerization pressure		Polymerization result			
	Hydrogen kg/cm ²	Ethylene kg/cm ²	Yield g	Catalyst efficiency	MI	FR
Al(i-C ₄ H ₉) ₃ (0.5)	1.3	2.7	327	24,200	6.1	30
Al(C ₆ H ₁₇) ₃ (2.0)	1.0	3.0	325	21,700	4.5	27
Al(n-C ₃ H ₇) ₃ (1.0)	1.0	3.0	264	17,600	3.5	25
Al(i-C ₄ H ₉) ₃ (0.5)	1.3	2.7	286	21,200	6.8	27
Al(C ₂ H ₅) _{2.5} (OC ₂ H ₅) _{0.5} (2.0)	1.3	2.7	259	19,200	7.2	26
Al(i-C ₄ H ₉) ₃ (0.5)	0.7	3.3	343	29,700	2.1	26

WHAT WE CLAIM IS:—

1. A catalyst for the polymerization of ethylene or propylene or the copolymerization thereof with another olefin, the catalyst being prepared by forming a hydrocarbon insoluble product (A) by reacting: either

(i) a hydrocarbon-soluble organoaluminum-magnesium complex represented by the general formula $Al_nMg_sX_pY_qR^1R^2$ wherein R^1 and R^2 are each a hydrogen atom or a hydrocarbon radical having 1—10 carbon atoms; X and Y are the same or different and selected from OR³ or OSiR⁴R⁵R⁶ wherein R^3 is a hydrocarbon radical having 1—10 carbon atoms; R^4 , R^5 and R^6 are each a hydrogen atom or a hydrocarbon radical having 1—12 carbon atoms; α and β are each a number more than zero, $\beta/\alpha=1—10$, $p+q+r+s=3\alpha+2\beta$ and $0 < (p+q)/(\alpha+\beta) \leq 0.80$, or

(ii) a reaction product of a complex having the general formula of $Al_nMg_sR^1R^2$, which corresponds to $p+q=0$ in the general formula (i), with a linear or cyclic siloxane compound having a constitutional unit of

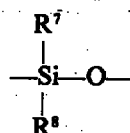


(wherein R^7 and R^8 are each a hydrogen atom or a hydrocarbon radical having 1—10 carbon atoms),

with (iii) one or more titanium or vanadium compounds having at least one halogen atom, and subsequently reacting the thus obtained hydrocarbon-insoluble reaction product (A) with an organoaluminum compound (B) represented by the general formula AlR^9Z_{3-m} wherein R^9 is a hydrocarbon radical having 1—20 carbon atoms; Z is selected from a hydrogen atom, halogen atom, alkoxy group, aryloxy group and siloxy group; and m is a number in the range 2—3.

2. A catalyst according to Claim 1 wherein reaction product (A) is formed from a hydrocarbon-soluble complex containing an organomagnesium bond, and having the general formula of $Al_nMg_sX_pY_qR^1R^2$ (wherein R^1 , R^2 , X, Y, α , β , p, q, r, and s are as defined in claim 1).

3. A catalyst according to claim 1 wherein reaction product (A) is formed from the reaction product of an organoaluminum-magnesium complex having the general formula $Al_nMg_sR^1R^2$ (wherein R^1 , R^2 , α , β , r, and s are as defined in claim 1) with a linear or cyclic siloxane compound having one or more units having the general formula of





2723

1,503,779

14

TABLE 5 (Continued)

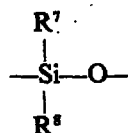
Catalyst	Polymerization pressure	Polymerization result				
		Hydrogen kg/cm ²	Ethylene kg/cm ²	Yield g	Catalyst efficiency	MI FR
Al(i-C ₄ H ₉) ₃ (0.5)		1.3	2.7	327	24,200	6.1 30
Al(C ₂ H ₅) ₃ (2.0)		1.0	3.0	325	21,700	4.5 27
Al(n-C ₃ H ₇) ₃ (1.0)		1.0	3.0	264	17,600	3.5 25
Al(i-C ₄ H ₉) ₃ (0.5)		1.3	2.7	286	21,200	6.8 27
Al(C ₂ H ₅) _{2.5} (OC ₂ H ₅) _{0.5} (2.0)		1.3	2.7	259	19,200	7.2 26
Al(i-C ₄ H ₉) ₃ (0.5)		0.7	3.3	343	29,700	2.1 26

WHAT WE CLAIM IS:—

1. A catalyst for the polymerization of ethylene or propylene or the copolymerization thereof with another olefin, the catalyst being prepared by forming a hydrocarbon insoluble product (A) by reacting: either

(i) a hydrocarbon-soluble organoaluminum-magnesium complex represented by the general formula $Al_nMg_sX_pY_qR^1R^2$ wherein R^1 and R^2 are each a hydrogen atom or a hydrocarbon radical having 1—10 carbon atoms; X and Y are the same or different and selected from OR^3 or $OSiR^4R^5R^6$ wherein R^3 is a hydrocarbon radical having 1—10 carbon atoms; R^4 , R^5 and R^6 are each a hydrogen atom or a hydrocarbon radical having 1—12 carbon atoms; α and β are each a number more than zero, $\beta/\alpha=1-10$, $p+q+r+s=3\alpha+2\beta$ and $0 < (p+q)/(\alpha+\beta) \leq 0.80$, or

(ii) a reaction product of a complex having the general formula of $Al_nMg_sR^1R^2$, which corresponds to $p+q=0$ in the general formula (i), with a linear or cyclic siloxane compound having a constitutional unit of

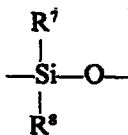


(wherein R^7 and R^8 are each a hydrogen atom or a hydrocarbon radical having 1—10 carbon atoms).

with (iii) one or more titanium or vanadium compounds having at least one halogen atom, and subsequently reacting the thus obtained hydrocarbon-insoluble reaction product (A) with an organoaluminum compound (B) represented by the general formula AlR^3Z_{3-m} wherein R^3 is a hydrocarbon radical having 1—20 carbon atoms; Z is selected from a hydrogen atom, halogen atom, alkoxy group, aryloxy group and siloxy group; and m is a number in the range 2—3.

2. A catalyst according to Claim 1 wherein reaction product (A) is formed from a hydrocarbon-soluble complex containing an organomagnesium bond, and having the general formula of $Al_nMg_sX_pY_qR^1R^2$ (wherein R^1 , R^2 , X, Y, α , β , p, q, r, and s are as defined in claim 1).

3. A catalyst according to claim 1 wherein reaction product (A) is formed from the reaction product of an organoaluminum-magnesium complex having the general formula $Al_nMg_sR^1R^2$ (wherein R^1 , R^2 , α , β , r, and s are as defined in claim 1) with a linear or cyclic siloxane compound having one or more units having the general formula of





(wherein R^7 , R^8 are as defined in claim 1) in the form of a dimer or a polymer greater than dimer.

4. A catalyst according to claim 1 wherein X and Y of said organoaluminum-magnesium complex represented by the general formula of $Al_nMg_pX_qY_rR^1R^2$ are each an alkoxy radical or an aryloxy radical.

5. A catalyst according to Claim 1 wherein X and Y of said organoaluminum-magnesium complex represented by the general formula of $Al_nMg_pX_qY_rR^1R^2$ are siloxy radicals represented by the general formula of $OSiR^4R^5R^6$.

6. A catalyst according to claim 1, 4 or 5 wherein β/α of said organoaluminum-magnesium complex represented by the general formula of $Al_nMg_pX_qY_rR^1R^2$ is in the range of 2-6.

7. A catalyst according to Claim 1, 4 or 5, wherein $(p+q)/(\alpha+\beta)$ of said organoaluminum-magnesium complex of $Al_nMg_pX_qY_rR^1R^2$ is in the range of 0.30-0.80.

8. A catalyst according to any one of claims 1 to 7, wherein titanium or vanadium compound is titanium tetrachloride, monobutoxytitanium trichloride, monopropoxytitanium trichloride, monoethoxytitanium trichloride, vanadium tetrachloride, vanadyl trichloride or mixtures of the above-mentioned compounds.

9. A catalyst according to any one of claims 1 to 8, wherein said organoaluminum-magnesium complex is reacted with said titanium or vanadium compound at a temperature lower than 20°C.

10. A catalyst according to any one of claims 1 to 9, wherein said organoaluminum-magnesium complex component and titanium or vanadium compound component are simultaneously added to a reaction zone to form reaction product A.

11. A catalyst according to any one of claims 1 to 10 wherein said organoaluminum-magnesium complex is reacted with said titanium or vanadium compound in a ratio of 0.2-5 mols of the former to one mol of the latter.

12. A catalyst according to any one of claims 1 to 11 wherein said organoaluminum compound represented by the general formula of $AlR^3_mZ_{3-m}$ is trialkyl aluminum or dialkyl aluminum hydride.

13. A catalyst according to any one of claims 1 to 12 wherein said component (B) is reacted with said component (A) in a ratio of 1-3,000 m mols of said component (B) to 1 g of said component (A).

14. A catalyst according to Claim 1 substantially as described in any one of the Examples.

15. A process for polymerizing ethylene or propylene or copolymerizing ethylene or propylene with another olefin which comprises performing the polymerization in the presence of a catalyst according to any one of claims 1 to 14.

16. A process according to claim 15 substantially as described in any one of the Examples.

17. A polymer or copolymer produced by a process according to claim 15 or 16.

BROOKES & MARTIN,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London WC1V 6SE.
Agents for the Applicants.