(54) Heat treatment of ziegler-natta catalysts to increase polymer molecular weight in solution polymerization
Wärmebehandlung von Ziegler-Katalysatoren zur Erhöhung des Polymermolekulargewichts in der Polymerisationslösung
Traitement de chauffage des catalyssateurs de Ziegler Natta pour augmenter le poids moléculaire du polymère dans la solution de polymérisation

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The present invention relates to a process for the heat treatment of Ziegler-Natta catalyst systems which also contain magnesium.

United States patents 5,589,555 (Zboril et al. issued December 31, 1996) and 5,519,098 (Brown et al. issued May 21, 1996), both assigned to Novacor Chemicals (International) S.A. (now NOVA Chemicals (International) S.A.), disclose catalysts for the solution polymerization of alpha-olefins. The patents disclose a catalyst system comprising:

(i) a mixture of a trialkyl aluminum compound and a dialkyl magnesium compound;
(ii) a reactive chloride which may be an alkyl halide;
(iii) a transition metal compound; and
(iv) the reaction product of a trialkyl aluminum compound and an alcohol in amounts up to about stoichiometric amounts to produce a dialkyl aluminum alkoxide.

The present invention has removed the step in the process of the above patents of the reaction of a trialkyl aluminum compound with an alcohol. Additionally the patent teaches against the subject matter of the present patent application as the patent teaches cooling the precursor for a period of time from 5 seconds to 60 minutes then heating the catalyst.

United States patent 4,097,659 issued June 27, 1978 to Creemers et al., assigned to Stamicarbon, N.V., now expired, discloses a process for producing polyolefins in which a precursor is prepared by reacting an aluminum alkyl halide of the formula RmAlX3-m with an organomagnesium compound of the formula MgR'2 wherein m is a value less than 3, that is the aluminum compound may have 1, 2 or 3 halogen atoms; and R and R' independently may be a C1 to C30 hydrocarbyl radical. The Creemers patent does not teach or suggest that the first component could be the reaction product of a trialkyl aluminum compound and a dialkyl magnesium compound. In fact the patent teaches against such a system as illustrated by the comparative example in which the first component is prepared by reacting trimethyl aluminum and dibutyl magnesium. The resulting reaction product is then reacted with a transition metal compound. The resulting precursor is then activated with an organoaluminum activator selected from the group consisting of trialkyl aluminum and dialkyl magnesium. The Creemers patent does not teach or suggest that the first component could be a dialkyl aluminum alkoxide. Further, like Brown, Creemers suggests cooling the step in the process when the aluminum compound is reacted with the magnesium compound. In short the patent teaches away from the subject matter of the present invention.

United States patent 4,314,912 issued February 9, 1982 to Lowery, Jr. et al., assigned to The Dow Chemical Company, teaches a catalyst which is a reaction product of a transition metal, an organomagnesium compound, and a non-metallic monohalide. In the catalyst the ratio of Mg:transition metal is about 16:1 which is well below the amount specified in the Lowery patent. Lowery teaches mixing the catalyst components at a temperature from about -50°C to 150°C but that the period of time for mixing the components is not critical as the reaction occurs within one minute. Lowery teaches away from the subject matter of the present invention.

United States patent 4,431,784 issued February 14, 1984 to Hamilton et al. teaches the heat treatment of a catalyst. The catalyst is prepared by mixing the first two components (i.e. an organoaluminum and a titanium compound) at a temperature below ambient (30°C) and then heating the resulting mixture to a temperature from 150°C to 300°C for a period of time from 10 seconds to 10 minutes. Then a subsequent aluminum compound is added to the reactants and the catalyst is complete. In addition to teaching a different temperature cycle Hamilton teaches a catalyst which does not contain any magnesium compound.

Generally, in the continuous solution polymerization process of ethylene higher catalyst activity leading to increased ethylene conversion results in a decrease in polymer molecular weight (e.g. Mw). This is a challenge to the industry to increase both the activity of the catalyst as well as the resulting polymer molecular weight or to maintain catalyst activity and increase resulting polymer molecular weight. In a manufacturing situation this may lead to a dynamic between maintaining high production rates and simultaneously obtaining useful high molecular weight products. Obtaining low molecular weight products is not challenging in a higher temperature solution process.

The present invention seeks to provide a catalyst useful in high temperature solution polymerization which provides a high activity catalyst which yields a substantial improvement in the molecular weight (in the order of up to 80%) for ethylene copolymers. For ethylene homopolymers the catalysts provide a moderate improvement in molecular weight without any loss in activity. This is unusual as generally an increase in molecular weight typically may result in a decrease in reactivity.

Accordingly, the present invention seeks to provide a process to prepare a catalyst for the solution polymerization of ethylene...
The present invention is directed to a process for the preparation of useful polymers of alpha-olefins, such polymers being intended for fabrication into articles by extrusion, injection molding, rotational molding and the like. In particular, the polymers of alpha-olefins are homopolymers of ethylene and copolymers of ethylene and higher alpha-olefins, i.e. alpha-olefins of the ethylene series, especially such higher alpha-olefins having 3 to 12 carbon atoms, i.e. C_{3-12} alpha-olefins, examples of which include 1-butene, 1-hexene, and 1-octene. The preferred higher alpha-olefins have 4-10 carbon atoms. In addition cyclic endomethlenic dienes may be fed to the process with the ethylene or mixtures of ethylene and C_{3-12} alpha-olefin. The monomer feed typically comprises at least 40 weight % of ethylene and up to 60 weight % of one or more comonomers selected from the group consisting of C_{3-12} alpha-olefins, and higher alpha-olefins, i.e. alpha-olefins of the ethylene series, especially such higher alpha-olefins having 3 to 12 carbon atoms, i.e. C_{3-12} alpha-olefins, examples of which include 1-butene, 1-hexene, and 1-octene. The preferred higher alpha-olefins have 4-10 carbon atoms. In addition cyclic endomethlenic dienes may be fed to the process with the ethylene or mixtures of ethylene and C_{3-12} alpha-olefin. The monomer feed typically comprises at least 40 weight % of ethylene and up to 60 weight % of one or more comonomers selected from the group consisting of C_{3-12} alpha-olefins. Such polymers are known per se.

In the process of the present invention, monomer, generally one or more hydrocarbyl monomers, a coordi-
nation catalyst and inert hydrocarbon solvent, and optionally, hydrogen, are fed to a reactor. The monomer may be ethylene or mixtures of ethylene and at least one C₃₋₁₂ alpha-olefin, preferably ethylene or mixtures of ethylene and at least one C₄₋₁₀ alpha-olefin.

[0015] The solvent used in the preparation of the coordination catalyst is an inert C₆₋₁₀ hydrocarbon which may be unsubstituted or substituted by a C₁₋₄ alkyl radical, such as a hydrocarbon that is inert with respect to the coordination catalyst. Such solvents are known and include for example, hexane, heptane, octane, cyclohexane, methycyclohexane, and hydrogenated naphtha. The solvent used in the preparation of the catalyst is preferably the same as that fed to the reactor for the polymerization process. Caution should be exercised in selecting a solvent as a saturated monomer is not desired as a solvent for the reaction (i.e. hexane would not be preferred solvent for a hexene-containing monomer).

[0016] The process of the present invention may be practiced over a wide range of temperatures that may be used in an alpha-olefin polymerization process operated under solution conditions. For example such polymerization temperatures may be in the range of 105°C to 320°C, preferably in the range of 130°C to 250°C, most preferably in the range from 140°C to 230°C. However, one of the considerations in selecting the temperature is that the polymer should remain in solution.

[0017] The pressures used in the process of the present invention are those known for solution polymerization processes, for example, pressures in the range of about 4 to 20 MPa, preferably from 8 to 20 MPa.

[0018] In the process of the present invention, the alpha-olefin monomers are polymerized in the reactor in the presence of the catalyst. Pressure and temperature are controlled so that the polymer formed remains in solution.

[0019] Optionally, small amounts of hydrogen, for example 0 - 100 parts per million, based on the total solution fed to the reactor, may be added to the feed in order to improve control of the melt index and/or molecular weight and thus aid in the production of a more uniform product, as is disclosed in Canadian Patent 703,704.

[0020] The catalysts of the present invention have improved activity over prior Mg/Al/Ti catalysts and particularly those used in solution processes at temperatures between 105°C and 320°C. The catalyst activity is defined as:

\[
K_p = \frac{(Q/(1-Q))(1/HUT)(1/catalyst concentration)}
\]

wherein:

\( Q \) is the fraction of ethylene monomer converted;
\( HUT \) is the reactor hold-up time expressed in minutes; and
the catalyst concentration is the concentration in the polymerization reactor expressed in mmol/l.

[0021] The coordination catalyst is formed from four components.

[0022] The first component is a mixture of an alkyl aluminum compound of the formula (R¹)₃Al wherein R¹ is a C₁₋₁₀, preferably a C₁₋₄ alkyl radical and a dialkyl magnesium compound of the formula (R²)₂Mg wherein each R² is independently (i.e. each R² may be the same or different) a C₁₋₁₀, preferably a C₂₋₆, alkyl radical. The molar ratio of Mg to Al¹ in the first component may be from 4:1 to 8:1 preferably from 6:1 to 8:1. In a particularly preferred embodiment of the present invention the aluminum compound is triethyl aluminum.

[0023] The second component in the catalyst systems according to the present invention is a reactive alkyl halide (reactive halide) of the formula R³X wherein R³ is a C₁₋₄, preferably a C₁₋₄, alkyl radical and X is a halide selected from the group consisting of chlorine and bromine. Preferably, the second component is t-butyl halide, most preferably t-butyl chloride.

[0024] The third component in the catalyst of the present invention is the transition metal halide TiCl₄. In the catalysts of the present invention the molar ratio of Mg: Ti is from 4:1 to 8:1, preferably from 6:1 to 8:1.

[0025] The fourth component in the catalyst of the present invention is an alkyl aluminum alkoxide of the formula (Rⁿ)₂AlOR wherein Rⁿ and OR are independently selected from the group consisting of C₁₋₄, preferably C₁₋₄ alkyl radicals. A useful dialkyl aluminum alkoxide is diethyl aluminum ethoxide.

[0026] The components of the catalyst system are mixed to provide a molar ratio of Mg: Ti from 4:1 to 8:1, preferably from 6:1 to 8:1; a molar ratio of Al¹ (e.g. aluminum alkyl) to TiCl₄ from 0.9:1 to 1.5:1, preferably from 1:1 to 1.3:1; a molar ratio of (reactive) halide to Mg from 1:1 to 2.6:1, preferably from 1.9:1 to 2.5:1 and a molar ratio of Al² (alkyl aluminum alkoxide) to titanium from 2:1 to 4:1, preferably from 3:1 to 4:1.

[0027] Two of the four components of the catalyst system are mixed together at once, generally the first components (e.g. the mixture of Al¹ and Mg and the reactive halide (t-butyl halide)) are mixed together, and heated at a temperature from 40°C to 70°C, for a time from 2 to 15 minutes, preferably from 5 to 10 minutes. One of components (iii) and (iv) may be added to the transfer line between the first and second reactor, and the other component may be added directly to the second reactor.
The catalyst system of the present invention is used in the process of the invention without separation of any of the components of the catalyst. In particular, neither liquid nor solid fractions are separated from the catalyst before it is fed to the reactor. In addition, the catalyst and its components are not slurries. All the components are easy-to-handle, storable, stable liquids.

The solvent containing monomers, catalyst or catalyst components, and optionally hydrogen are fed to the reactor and react under good mixing conditions for a short period of time, preferably less than 10 minutes.

The solution passing from the polymerization reactor is normally treated to deactivate any catalyst remaining in the solution. A variety of catalyst deactivators are known, examples of which include fatty acids, alkaline earth metal salts of aliphatic carboxylic acids and alcohols. The hydrocarbon solvent used for the deactivator is preferably the same as the solvent used in the polymerization process. If a different solvent is used, it must be compatible with the solvent used in the polymerization mixture and not cause adverse effects on the solvent recovery system associated with the polymerization process. The solvent may then be flashed off from the polymer, which subsequently may be extruded into water and cut into pellets or other suitable comminuted shapes. The recovered polymer may then be treated with saturated steam at atmospheric pressure to, for example, reduce the amount of volatile materials and improve polymer color. The treatment may be carried out for about 1 to 6 hours, following which the polymer may be dried and cooled with a stream of air for 1 to 4 hours.

Pigments, antioxidants, UV screeners, hindered amine light stabilizers and other additives may be added to the polymer either before or after the polymer is formed into pellets or other comminuted shapes. The antioxidant incorporated into polymer obtained from the process of the present invention may, in embodiments, be a single antioxidant, e.g. hindered phenolic antioxidant, or a mixture of antioxidants, e.g. a hindered phenolic antioxidant combined with a secondary antioxidant, e.g. phosphite. Both types of antioxidant are known in the art. For example the ratio of phenolic antioxidant to secondary antioxidant may be in the range of 0.1:1 to 5:1 with the total amount of antioxidant being in the range of 200 to 3000 ppm.

The present invention will now be illustrated by the following nonlimiting examples. Unless otherwise indicated, parts means part by weight and percent (%) is weight percent. In the following examples unless indicated otherwise the compound to give Al1 was triethyl aluminum; the magnesium compound was n-dibutyl magnesium; the transition metal compound was TiCl4; the halide compound was t-butyl chloride; and the compound providing the Al2 was diethyl aluminum ethoxide.

Example 1

The following examples were conducted in a small-scale continuous polymerization unit. In the examples both homo- and copolymers were prepared. The catalyst in accordance with the present invention was prepared by feeding two of the four components in a first continuous stirred tank reactor. The third and fourth components were either added at the exit of the first reactor or directly to the second continuous stirred reactor. The monomer(s) were fed continuously to the second continuous reactor. In the experiments the second continuous reactor was operated at a temperature of about 200°C. The temperature of the first continuously stirred reactor is specified in Table 1 below. In the experiments the catalyst for the homopolymer and copolymer were prepared using the same conditions. For convenience, the catalyst mixing temperature for both the homopolymer and copolymer runs is listed in the first column. For each run (homopolymer and copolymer) the catalyst reactivity (Kp) and the density and molecular weight for the resulting polymer was measured. In the experiments the transition metal was TiCl4; the halide was t-butyl chloride; the first aluminum (Al1) compound was triethyl aluminum mixed with di-n-butyl magnesium (Magala); and the second aluminum compound (Al2) was diethyl aluminum ethoxide.
Polymer weight average molecular weight (Mw) was determined by Gel Permeation Chromatography (GPC).
Runs #1 and 6 (Control):

[0035] All catalyst components were fed continuously, mixed in line (without heating) for about 30 - 120 seconds. Catalyst molar ratios: Mg/Ti = 7.68, Mg/Al1 = 7.68, Cl/Mg = 2.0, Al1/Ti = 1.0 and Al2/Ti = 3.0.

Runs # 2, 3, 7 and 8:

[0036] The Magala, (R1)2Al1 and (R2)2Mg mixture and the halide R3X were mixed in continuous stirred reactor for 10 minutes. The transition metal (TiCl4) was added to transfer line and the second aluminum compound (R4)2Al2OR5 was fed separately to polymerization reactor which was at 200°C.

[0037] The catalysts for runs # 4, 5, 9 and 10 were prepared as in runs # 2 and 3 except that the catalyst mixing and heating time in the first reactor was 2.3 minutes.

Runs 2 to 10:

[0038] Catalyst molar ratios: Mg/Ti = 6.87, Mg/Al1 = 6.87, Cl/Mg = 2.0, Al1/Ti = 1.0 and Al2/Ti = 3.0.

[0039] The above examples show that runs 2, 3, 7 and 8 wherein (R1)2Al1 and (R2)2Mg mixture and R3X mixed and heated for 10 minutes lead to increase in the homopolymer molecular weight, without loss in the catalyst activity (Kp). Consequently, when (R1)2Al1 and (R2)2Mg mixture and R3X halide are heated between 40 - 70°C for 10 minutes it is shown to be the most preferred catalyst preparation method to lead to high copolymer molecular weight.

Claims

1. A process to prepare a catalyst for the solution polymerization of a mixture of one or more linear C2-12 alpha-olefins at a temperature from 105°C to 320°C and a pressure from 4 to 20 MPa wherein said catalyst comprises:

   (i) a mixture of an alkyl aluminum compound of the formula (R1)2Al1 and (R2)2Mg wherein R1 is a C1-10 alkyl radical and R2 is a C1-10 alkyl radical in a molar ratio of Mg to Al1 from 4.0:1 to 8:1;

   (ii) a halide of the formula R3X wherein R3 is selected from the group consisting of C1-8 alkyl radicals and X is selected from the group consisting of chlorine and bromine;

   (iii) titanium tetrachloride; and

   (iv) an alkyl aluminum alkoxide compound of the formula (R4)2Al2OR5 wherein R4 and R5 are independently selected from the group consisting of C1-10 alkyl radicals,

   to provide a molar ratio of Mg:Ti from 4:1 to 8:1; a molar ratio of Al1 to titanium tetrachloride from 0.9:1 to 1.5:1; a molar ratio of halide to Mg from 1.9:1 to 2.6:1; and a molar ratio of Al2 to titanium from 2:1 to 4:1 comprising mixing in an inert hydrocarbon in a first reactor components (i) and (ii) and maintaining them at a temperature from 30°C to 70°C for a period of time from 2 to 15 minutes and adding the remaining catalyst components to the heat treated mixture, to the second reactor, or both.

2. The process according to claim 1, wherein the mole ratio of Al1 to TiCl4 is from 1:1 to 1.3 to 1.

3. The process according to either claim 1 or claim 2, wherein the mole ratio of halide to Mg is from 1.9:1 to 2.5:1.

4. The process according to any one of claims 1 to 3, wherein the mole ratio of Mg to Al1 is from 6:1 to 8:1.

5. The process according to any one of claims 1 to 4, wherein the mole ratio of Mg to Ti is from 6:1 to 8:1.

6. The process according to any one of claims 1 to 5, wherein the mole ratio of Al1 to Ti is from 0.9:1 to 1.1 to 1.

7. The process according to any one of claims 1 to 6, wherein the mole ratio of Al2 to Ti is from 3:1 to 4:1.

8. The process according to any one of claims 1 to 7 wherein the time is from 5 to 10 minutes.

9. The process according to any one of claims 1 to 8, wherein R1, R3, R4 and R5 are independently selected from the group consisting of C1-4 alkyl radicals.
10. The process according to claim 9, wherein \( R^1 \) is an ethyl radical.

11. The process according to either claim 9 or claim 10 wherein \( R^2 \) is a \( C_{2-6} \) alkyl radical.

12. The process according to any one of claims 9 to 11, wherein \( R^3 \) is a tertiary butyl radical.

13. The process according to any one of claims 9 to 12, wherein \( R^4 \) and \( R^5 \) are ethyl radicals.

14. The process according to any one of claims 1 to 7 or claim 13 wherein \( TiCl_4 \) is added to the transfer line between the first and second reactor.

15. The process according to claim 14, wherein the \( Al^2 \) compound is added directly to the second reactor.

16. The process according to any one of claims 1 to 7 or claim 13 wherein the \( Al^2 \) compound is added to the transfer line between the first and second reactor.

17. The process according to claim 16, wherein the \( TiCl_4 \) compound is added directly to the second reactor.

18. A process for the solution polymerization of a mixture comprising at least 40 weight % of ethylene and up to 60 weight % of one or more \( C_{3-12} \) alpha-olefins at a temperature from 105 °C to 320 °C and a pressure from 4 to 20 MPa in a chain of at-least two continuous stirred reactors connected in series where the first reactor is used to react catalyst components and the subsequent reactors are for polymerization and the catalyst is prepared according to any one of the preceding claims.

Patentansprüche

1. Verfahren zur Herstellung eines Katalysators zur Lösungspolymerisation eines Gemischs aus einem oder mehre-  
en linearen \( C_{2-12} \)-\( \alpha \)-Olefinen bei einer Temperatur von 105 °C bis 320 °C und einem Druck von 4 bis 20 MPa,  
woin der Katalysator Folgendes umfasst:

   (i) ein Gemisch aus einer Alkylaluminiumverbindung der Formel \( (R^1)_3Al \) und \( (R^2)_2Mg \), worin \( R^1 \) ein \( C_{1-10} \)-Alkylrest ist und \( R^2 \) ein \( C_{1-10} \)-Alkylrest ist, in einem Molverhältnis zwischen Mg und Al von 4,0:1 bis 8:1;

   (ii) ein Halogenid der Formel \( R^3 X \), worin \( R^3 \) aus der aus \( C_{1-8} \)-Alkylresten bestehenden Gruppe ausgewählt ist und X aus der aus Chlor und Brom bestehenden Gruppe ausgewählt ist;

   (iii) Titantetrachlorid; und

   (iv) eine Alkylaluminiumalkoxidverbindung der Formel \( (R_4)_2Al_2OR_5 \), worin \( R^4 \) und \( R_5 \) unabhängig voneinander aus der aus \( C_{1-10} \)-Alkylresten bestehenden Gruppe ausgewählt sind,

   um ein Molverhältnis Mg:Ti von 4:1 bis 8:1; ein Molverhältnis zwischen Al und Titantetrachlorid von 0,9:1 bis 1,5:1; ein Molverhältnis zwischen Halogenid und Mg von 1,9:1 bis 2,6:1; und ein Molverhältnis zwischen Al und Titan von 2:1 bis 4:1 bereitzustellen, umfassend das Vermischen der Komponenten (i) und (ii) in einem inerten Kohlenwasserstoff in einem ersten Rektor, wobei sie für einen Zeitraum von 2 bis 15 Minuten bei einer Temperatur von 30 °C bis 70 °C gehalten werden, und das Zusetzen der übrigen Katalysatorkomponenten zum wärmebehan-  
delten Gemisch, zum zweiten Rektor oder zu beiden.

2. Verfahren nach Anspruch 1, worin das Molverhältnis zwischen Al und \( TiCl_4 \) 1:1 bis 1,3:1 beträgt.

3. Verfahren nach Anspruch 1 oder Anspruch 2, worin das Molverhältnis zwischen Halogenid und Mg 1,9:1 bis 2,5:  
obeträgt.

4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Molverhältnis zwischen Mg und Al 6:1 bis 8:1 beträgt.

5. Verfahren nach einem der Ansprüche 1 bis 4, worin das Molverhältnis zwischen Mg und Ti 6:1 bis 8:1 beträgt.

6. Verfahren nach einem der Ansprüche 1 bis 5, worin das Molverhältnis zwischen Al und Ti 0,9:1 bis 1,1:1 beträgt.

7. Verfahren nach einem der Ansprüche 1 bis 6, worin das Molverhältnis zwischen Al und Ti 3:1 bis 4:1 beträgt.
8. Verfahren nach einem der Ansprüche 1 bis 7, worin der Zeitraum 5 bis 10 Minuten beträgt.

9. Verfahren nach einem der Ansprüche 1 bis 8, worin R¹, R³, R⁴ und R⁵ unabhängig voneinander aus der aus C₁-₄-Alkylresten bestehenden Gruppe ausgewählt sind.

10. Verfahren nach Anspruch 9, worin R¹ ein Ethylrest ist.

11. Verfahren nach Anspruch 9 oder 10, worin R² ein C₂₋₆-Alkylrest ist.

12. Verfahren nach einem der Ansprüche 9 bis 11, worin R³ ein tert-Butylrest ist.

13. Verfahren nach einem der Ansprüche 9 bis 12, worin R⁴ und R⁵ Ethylreste sind.

14. Verfahren nach einem der Ansprüche 1 bis 7 oder Anspruch 13, worin TiCl⁴ in die Überweisungsleitung zwischen dem ersten und dem zweiten Reaktor zugeführt wird.

15. Verfahren nach Anspruch 14, worin die Al²-Verbindung direkt dem zweiten Reaktor zugeführt wird.

16. Verfahren nach einem der Ansprüche 1 bis 7 oder Anspruch 13, worin die Al²-Verbindung in die Überweisungsleitung zwischen dem ersten und dem zweiten Reaktor zugeführt wird.

17. Verfahren nach Anspruch 16, worin die TiCl₄-Verbindung direkt dem zweiten Reaktor zugeführt wird.


Revendications

1. Procédé pour préparer un catalyseur pour la polymérisation en solution d'un mélange d'une ou plusieurs α-oléfines en C₂ à C₁₂ linéaires à une température de 105°C à 320°C et sous une pression de 4 à 20 MPa, dans lequel ledit catalyseur comprend :

   (i) un mélange d'un composé alkyl-aluminium de formules (R¹)₂Al₁ et (R²)₂Mg où R¹ est un radical alkyle en C₁ à C₁₀ et R² est un radical alkyle en C₁ à C₁₀ en un rapport molaire du Mg au Al₁ de 4,0/1 à 8/1 ;
   (ii) un halogénure de formule R³X où R³ est choisi dans l'ensemble constitué par les radicaux alkyle en C₁ à C₁₀ et X est choisi dans l'ensemble constitué par le chlore et le brome ;
   (iii) du tétrachlorure de titane ; et
   (iv) un composé alkylate d'alkyl-aluminium de formule (R⁴)₂Al²OR₅ où R⁴ et R⁵ sont indépendamment choisis dans l'ensemble constitué par les radicaux alkyle en C₁ à C₁₀, de façon qu'on obtienne un rapport molaire Mg/Ti de 4/1 à 8/1 ; un rapport molaire du Al₁ au tétrachlorure de titane de 0,9/1 à 1,5/1 ; un rapport molaire de l'halogénure au Mg de 1,9/1 à 2,6/1 ; et un rapport molaire du Al² au titane de 2/1 à 4/1 ;

comprenant le mélange dans un hydrocarbure inerte, dans une première réaction, des composants (i) et (ii), et le maintien de ceux-ci à une température de 30°C à 70°C pendant une période de temps allant de 2 à 15 minutes, et ensuite l'addition des composants de catalyseur restants au mélange traité chauffé, dans un deuxième réacteur, ou les deux.

2. Procédé selon la revendication 1, dans lequel le rapport molaire du Al₁ au TiCl₄ est de 1/1 à 1,3/1.

3. Procédé selon l'une ou l'autre de la revendication 1 et de la revendication 2, dans lequel le rapport molaire de l'halogénure au Mg est de 1,9/1 à 2,5/1.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le rapport molaire du Mg au Al₁ est de 6/1 à 8/1.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le rapport molaire du Mg au Ti est de 6/1 à 8/1.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le rapport molaire du Al\(^1\) au Ti est de 0,9/1 à 1,1/1.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le rapport molaire du Al\(^2\) au Ti est de 3/1 à 4/1.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le temps va de 5 à 10 minutes.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel R\(^1\), R\(^3\), R\(^4\) et R\(^5\) sont indépendamment choisis dans l'ensemble constitué par les radicaux alkyle en C\(_1\) à C\(_4\).

10. Procédé selon la revendication 9, dans lequel R\(^1\) est un radical éthyle.

11. Procédé selon l'une ou l'autre de la revendication 9 et de la revendication 10, dans lequel R\(^2\) est un radical alkyle en C\(_2\) à C\(_6\).

12. Procédé selon l'une quelconque des revendications 9 à 11, dans lequel R\(^3\) est un radical butyle tertiaire.

13. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel R\(^4\) et R\(^5\) sont des radicaux éthyle.

14. Procédé selon l'une quelconque des revendications 1 à 7 et de la revendication 13, dans lequel du TiCl\(_4\) est ajouté dans la conduite de transfert entre le premier et le deuxième réacteurs.

15. Procédé selon la revendication 14, dans lequel le composé de Al\(^2\) est ajouté directement dans le deuxième réacteur.

16. Procédé selon l'une quelconque des revendications 1 à 7 et de la revendication 13, dans lequel le composé du Al\(^2\) est ajouté dans la conduite de transfert entre le premier et le deuxième réacteurs.

17. Procédé selon la revendication 16, dans lequel le composé du TiCl\(_4\) est ajouté directement dans le deuxième réacteur.

18. Procédé pour la polymérisation en solution d'un mélange comprenant au moins 40 % en poids d'éthylène et jusqu'à 60 % en poids d'une ou plusieurs α-oléfines en C\(_3\) à C\(_{12}\) à une température de 105°C à 320°C et sous une pression de 4 à 20 MPa, dans une chaîne d'au moins deux réacteurs agités en continu et connectés en série, où on utilise le premier réacteur pour faire réagir les composants de catalyseur et les réacteurs subséquents servent à la polymérisation et le catalyseur est préparé selon l'une quelconque des revendications précédentes.