Title: PROCESS FOR THE GAS-PHASE POLYMERIZATION OF OLEFINS

Abstract: A process for the gas-phase polymerization of α-olefins CH\textsubscript{2}=CHR, where R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, carried out in a first and a second interconnected polymerization zones, wherein the growing polymer particles flow through the first of said polymerization zones (riser) under fast fluidization conditions, leave said riser and enter the second of said polymerization zones (downcomer) through which they flow downward in a densified form, leave said downcomer and are reintroduced into said riser, in which process: (a) the gas mixture present in the riser is totally or partially prevented from entering the downcomer, and (b) the gaseous composition inside a portion of the downcomer is maintained substantially similar to the gaseous composition reacting in the riser.

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TITLE:

Process for the gas-phase polymerization of olefins

The present invention relates to a gas-phase polymerization process for the olefin polymerization carried out in a reactor having interconnected polymerization zones. In particular, the operative conditions selected in the polymerization process of the invention allow broadening the range of polymer compositions obtainable by means of a polymerization reactor having interconnected polymerization zones.

The development of olefin polymerization catalysts with high activity and selectivity, particularly of the Ziegler-Natta type and, more recently, of the metallocene type, has led to the widespread use on an industrial scale of processes in which the polymerization of olefins is carried out in a gaseous medium in the presence of a solid catalyst.

A widely used technology for gas-phase polymerization processes is the fluidized bed technology. In fluidized bed gas-phase processes, the polymer is confined in a vertical cylindrical zone. The reaction gases exiting the reactor are taken up by a compressor, cooled and sent back, together with make-up monomers and appropriate quantities of hydrogen, to the bottom of the bed through a distributor. Entrainment of solid in the gas is limited by an appropriate dimensioning of the upper part of the reactor (freeboard, i.e. the space between the bed surface and the gas exit point), where the gas velocity is reduced, and, in some designs, by the interposition of cyclones in the exit gas line. The flow rate of the circulating gas is set so as to assure a velocity within an adequate range above the minimum fluidization velocity and below the "transport velocity". The heat of reaction is removed exclusively by cooling the circulating gas. The composition of the gas-phase controls the composition of the polymer, while the reaction kinetics is controlled by the addition of inert gases. The reactor is operated at constant pressure, normally in the range 1-4 MPa.

A significant contribution to the reliability of the fluidized-bed reactor technology in the polymerization of α-olefins was made by the introduction of suitably pre-treated spheroid catalyst of controlled dimensions and by the use of propane as a diluent.

Since fluidized-bed reactors approximate very closely the ideal behaviour of a "continuous stirred-tank reactor" (CSTR), it is very difficult to obtain products which are a homogeneous mixture of different types of polymeric chains. In fact, the composition of the gaseous mixture that is in contact with the growing polymer particle is essentially the
same for all the residence time of the particle in the reactor. As a consequence, one of the major limits of fluidized-bed processes is the difficulty of broadening the molecular weight distribution of the obtained polymers. The broadness of the molecular weight distribution has an influence both on the rheological behaviour of the polymer (and hence the processability of the melt) and on the final mechanical properties of the product, and is a characteristic which is particularly important for (co)polymers based on ethylene or propylene.

This problem has been addressed in EP 782 587. According to this patent, it is possible to broaden the molecular weight distribution of polymers without affecting their homogeneity by means of a gas-phase process performed in a loop reactor responding to particular criteria of design. The gas-phase polymerization according to EP 782 587 is carried out in two interconnected polymerization zones to which one or more monomers are fed in the presence of a catalyst under reaction conditions and from which the polymer produced is discharged. The process is characterized in that the growing polymer particles flow through the first of said polymerization zones under fast fluidization conditions, leave said first polymerization zone and enter the second polymerization zone, through which they flow in a densified form under the action of gravity, leave the second polymerisation zone (hereinafter “downcomer”) and are reintroduced into the first polymerisation zone (hereinafter “riser”), thus establishing a circulation of polymer between the two polymerisation zones.

According to the teachings of EP 782 587, it is possible to broaden the molecular weight distribution of the polymers simply by properly balancing the gas-phase compositions and the residence times in the two polymerisation zones of the gas-phase loop reactor. This is due to the fact that, while the polymer moves downward in the second polymerization zone flowing in a plug-flow mode, owing to the monomer consumption, it finds gas-phase compositions richer in molecular weight regulator. Consequently, the molecular weights of the forming polymer decrease along the axis of this polymerisation zone.

However, the process described in EP 782 587 can provide only a limited control of the molecular weight distribution and is unable to prepare blends of two different (co)polymers. In fact, even if hindered by the presence of the packed polymer, the diffusion of the gas within the downcomer occurs, so that it is not possible to establish substantial differences in the monomer compositions between the riser and the downcomer.
An improvement over EP 782 587 is given by the polymerization process disclosed in EP 1012195, where the above described gas-phase reactor having interconnected polymerization zones is made more flexible and also suitable to the preparation of polymers endowed with broad composition distributions, while at the same time maintaining a high homogeneity level of the obtained polymer product. According to the teaching of EP 1012195, it is possible to obtain, within the reactor, two polymerization zones at different compositions by feeding a gas or liquid mixture to the top of the second polymerization zone. Said mixture acts as a barrier to the gas coming from the first polymerization zone. The introduction of the gas and/or liquid mixture of different composition in the second polymerization zone is such to establish a net gas flow upward at the upper limit of this polymerization zone. The established flow of gas upward has the effect of preventing the gas mixture present in the first polymerization zone from entering the second polymerization zone.

The embodiment disclosed in EP 1012195 is particularly useful to prepare bimodal homopolymers or copolymers, however the peculiar design of this gas-phase reactor, as well as the polymerization conditions established within the riser and the downcomer give rise to restrictions on the individual throughput of each polymerization zone.

Specifically, the polymer hold-up in the downcomer is poorly tunable due to the densified conditions of the polymer particles descending along this polymerization zone. The condition of packed flow of densified polymer makes it impossible increasing in a significant way the amount of polymer formed in this polymerization zone: in fact the solid density (kg of polymer per m$^3$ of reactor) inside the downcomer nearly approaches the bulk density of the formed polymer, so that this parameter cannot be further increased without clogging this polymerization zone. On the other hand, the density of solid cannot be significantly decreased, otherwise the densified conditions are not more satisfied and a steady recirculation of polymer throughout the reactor cannot be accomplished. As a consequence, the only parameter which is slightly changeable is the volume of polymer bed filling the downcomer: however, this parameter can be only slightly modified by varying the height of the polymer bed filling the downcomer to an extent not higher than 5%. Accordingly, the hold-up of (co)polymer produced in the downcomer can be varied of an amount not higher than 5% by weight.

As regards the first polymerization zone, the operative conditions of fast fluidizations of the polymer make the throughput of the riser more tunable with respect to the downcomer: the
polymer bed inside the riser can be rather diluted as well as slightly densified, while maintaining fast fluidization conditions. In particular, the density of solid in the riser can be ranged between a minimum value of about 50 Kg/m³ and a maximum value of about 250 Kg/m³, while maintaining fast fluidization conditions. On the other hand, the volume of polymer bed inside the riser cannot be modified, both the diameter and the height of the polymer bed inside the riser being fixed by the functional design of the reactor.

In view of the above technical considerations, when feeding a gas/liquid barrier of suitable composition to the top of the downcomer so as to differentiate the monomers composition in the riser from the monomers composition in the downcomer, the maximum split of (co)polymer obtainable from the riser is achieved by operating the riser with a density of solid of about 250 Kg/m³ and simultaneously by operating the downcomer according to a situation of minimum height of the densified polymer bed. However, even working according to this border-line condition, the split of polymer composition formed in the riser cannot overcome the amount of 60% by weight. As a consequence, some polymer compositions having a remarkable industrial interest, such as bimodal polyethylene blends or polypropylene blends, wherein one of the two polymeric components is present in an amount higher than 70% by weight, cannot be prepared according to the technical indications given in the above prior art patents. Furthermore, according to the current industrial techniques, such peculiar polyolefins blends are commonly prepared by using a sequence of two polymerization reactors, suitably tailoring the process conditions in each reactor to prepare a first polymer component in a first reactor and the second polymer component in the second reactor. However, these multistage polymerization processes lead to final (co)polymer blends suffering of a lack in homogeneity. In fact, in each reactor of said cascade-processes a different polymer is generated in term of molecular weight, chemical composition and cristallinity, so that the final polymer blend shows an intrinsic heterogeneity, caused by the inherent difference in the residence times of the polymer particles exiting each polymerization step.

In view of the above, it would be highly desirable to overcome the drawbacks of poor homogeneity given by the conventional multistage polymerization processes by modifying the polymerization process described in EP 1012195, so as to achieve a complete flexibility in the mutual ratio of the (co)polymer components, which are prepared in the interconnected polymerization zones.

It is therefore an object of the present invention a process for the gas-phase polymerization
of α-olefins CH$_2$=CHR, where R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, carried out in a first and a second interconnected polymerization zones, to which one or more of said α-olefins are fed in the presence of a catalyst under reaction conditions and from which the polymer product is discharged, wherein the growing polymer particles flow through the first of said polymerization zones (riser) under fast fluidization conditions, leave said riser and enter the second of said polymerization zones (downcomer) through which they flow downward in a densified form, leave said downcomer and are reintroduced into said riser, in which process:

(a) the gas mixture present in the riser is totally or partially prevented from entering the downcomer, and

(b) the gaseous composition inside a portion of the downcomer is maintained substantially similar to the gaseous composition reacting in the riser.

The operative conditions selected in the process according to the present invention allow widening the range of polymer compositions directly obtainable from a single gas-phase reactor having interconnected polymerization zones. By way of an example, bimodal polyethylene blends comprising the low molecular weight component in an amount higher than 70% by wt or, alternatively, polypropylene blends of a homopolymer and a random copolymer comprising a homopolymer component in an amount lower than 30% by wt, can be directly prepared and discharged from said gas-phase polymerization reactor.

A relevant advantage of the present invention is therefore obtaining the above polyolefin blends by means of a single gas-phase polymerization reactor, without any substantial limitation as regards the mutual ratio of the (co)polymer components contained in the polyolefin blends.

To produce the above polyolefin blends a gas-phase reactor having interconnected polymerization zones of the type described in EP 782 587 and EP 1012195 is exploited. In the first polymerization zone (riser), fast fluidization conditions are established by feeding a gas mixture comprising one or more α-olefins at a velocity higher than the transport velocity of the polymer particles. The velocity of said gas mixture is generally comprised between 0.5 and 15 m/s, preferably between 0.8 and 5 m/s. The terms "transport velocity" and "fast fluidization conditions" are well known in the art; for a definition thereof, see, for example, "D. Geldart, Gas Fluidisation Technology, page 155 et seq., J. Wiley & Sons Ltd., 1986".
In the second polymerization zone (downcomer), the polymer particles flow under the action of gravity in a densified form, so that high values of density of the solid are reached (mass of polymer per volume of reactor), which approach the bulk density of the polymer. In other words, the polymer flows vertically down through the downcomer in a plug flow (packed flow mode), so that only small quantities of gas are entrained between the polymer particles.

The operating parameters, such as temperature and pressure, are those that are usual in gas-phase catalytic polymerization processes. For example, in both the riser and downcomer the temperature is generally comprised between 50°C and 120°C, while the pressure can ranges from 0.5 to 10 MPa.

According to the process of the present invention the two interconnected polymerization zones are operated by satisfying both the conditions (a) and (b). In particular, the condition (a) requires the gas mixture coming from the riser to be partially or totally prevented from entering the downcomer. Conveniently, said condition can be achieved by introducing into the upper part of the downcomer a gas and/or liquid mixture having a composition different from the gaseous mixture present in the riser. One or more introduction lines, preferably placed at a point close to the upper limit of the volume occupied by the densified solid, can be used to this aim.

This gas/liquid mixture to be fed into the upper part of the downcomer partially or totally replaces the gas mixture entrained with the polymer particles entering the downcomer. The flow rate of this gas/liquid mixture can be regulated, so that a flow of gas counter-current to the flow of polymer particles is originated in the upper part of the downcomer, thus acting as a barrier to the gas mixture coming from the riser which is entrained among the polymer particles. The established flow of gas upward has the effect of preventing the gas mixture present in the riser from entering the downcomer.

The mixture of different composition to be fed at the upper part of the downcomer can be in a partially or totally liquefied form. The liquefied gas mixture can also be sprinkled over the upper surface of the bed of densified polymer particles; the evaporation of the liquid in the polymerization zone will provide the required gas flow.

Moreover, the above stated condition (b) requires maintaining inside a portion of the downcomer a gaseous composition which is substantially similar to the gaseous composition reacting in the riser. This means that, according to the invention, the molar amounts of the different gaseous components and/or their molar ratios are maintained
substantially at comparable values both in the riser and in a portion of the downcomer.
The effect of condition (b) is preparing inside a sub-portion of downcomer a (co)polymer
substantially similar to the (co)polymer produced in the riser. Conveniently, condition (b)
can be implemented by feeding a fluid of a suitable composition in correspondence of the
upper level of said portion of the downcomer. According to the present invention, said
fluid of a suitable composition can be either a gaseous mixture or a gas/liquid mixture.
Hereinafter, in the present description said fluid of a suitable composition fed into the
downcomer for satisfying the condition (b) will be referred with the term “corrective
fluid”.
The composition of this corrective fluid has to be suitably selected in order to obtain,
downstream its introduction point, a portion of downcomer characterized by a gas
composition substantially similar to the gas composition present in the riser. This means
that the mutual mixing between said corrective fluid and the gas flowing downwardly in
the downcomer is such to give, downstream the feeding point of said corrective fluid, a
gaseous mixture having substantially the same composition of the riser (condition b).
According to the present invention, the split of one of the two (co)polymer components
prepared by the polymerization process can be easily adjusted by rising or lowering along
the downcomer the feeding point of said corrective fluid. Therefore, the split of a
(co)polymer component prepared in the riser can be increased up to values in the order of
70-95% by weight.
The corrective fluid comes preferably from the recycle gas stream, which is continuously
recycled from the solid/gas separation zone placed at the top of the downcomer to the
bottom of the riser. As a consequence, said corrective fluid contains, besides the
monomers to be polymerized, also condensable inert compounds used as a polymerization
diluent: the preferred ones are aliphatic hydrocarbons C2-C8. Moreover, the composition of
said corrective fluid coming from the recycle gas line can be suitably adjusted by feeding
make-up monomers, polymerization diluents and hydrogen before its introduction into the
downcomer.
The process of the present invention will now be described in detail with reference to the
enclosed figure, which has to be considered illustrative and not limitative of the scope of
the invention.
Fig. 1 is a diagrammatic representation of the gas-phase polymerization process according
to the present invention.
The polymerization reactor comprises a riser 1 wherein the polymer particles flow upward under fast fluidization conditions and a downcomer 2, wherein the polymer particles flow downward under the action of gravity. The downcomer 2 comprises an upper area 2A marked by transversal lines and a bottom area 2B marked by crossed lines. The two polymerization zones 1 and 2 are appropriately interconnected by the sections 3 and 5. The catalyst components, preferably after a prepolymerization step, are continuously introduced via line 12 into the riser 1. A gaseous mixture comprising one or more olefins, hydrogen and optionally an alkane as a diluent gas is fed to the reactor via one or more lines 7, suitable placed at any point of the gas recycle line 6 according to the knowledge of those skilled in art.

The growing polymer particles and the gaseous mixture leaving the riser 1 are conveyed to a solid/gas separation zone 4, from which the polymer particles enter the downcomer 2. A gaseous mixture is collected in the upper portion of said separation zone 4, before entering the gas recycle line 6. This gaseous mixture is compressed by means of the compression means 8 and then split in two gaseous streams. The first one is cooled by the cooling device 9, and then fed to the connection zone 5 via line 10 and to the bottom of the riser 1 via line 11. The other gaseous stream, obtained downstream the compression means 8, is fed via line 14 to the condenser 15, where it is cooled to a temperature at which the monomers and optional condensable inert gases are partially condensed. A separating vessel 16 is placed downstream the condenser 15. The separated gaseous mixture, enriched in hydrogen, is send via line 17 to the recycle line 6. On the contrary, the liquid obtained from the condensation step is passed to line 18 before to be fed to the upper part of the downcomer 2. By means of line 18 the gas mixture present in the riser 1 is totally or partially prevented from entering the downcomer 2, thus carrying out the operative condition (a) of the present invention.

Simultaneously, a part of the recycle gas stream exiting the cooling device 9 is transferred to the downcomer 2 via line 19. Before the introduction into the downcomer the chemical composition of line 19 is suitable adjusted by feeding make-up monomers, inert diluents and hydrogen via line 20, so as to obtain the desired corrective fluid 21, as above defined. The feeding of said corrective fluid via line 21 makes the gaseous composition inside the portion 2B of the downcomer as much as possible similar to the gaseous composition present in the riser, thus implementing the operative condition (b) of the present invention.

The operative conditions (a) and (b) of the process of the invention allows preparing a first polymer component in the portion 2A of the downcomer, while a second polymer component
is formed inside the riser and the portion \textbf{2B} of the downcomer. The obtained polymer blend is then continuously discharged from the bottom of the downcomer via line 13. The polymerization process of the invention allows the preparation of a large number of polyolefin blends with a large flexibility as regards the mutual ratio of the (co)polymer components contained in the blend. In fact, the feeding of the corrective fluid at a higher point of the downcomer allows to enlarge the portion \textbf{2B}, thus increasing the percentage of the (co)polymer component formed in said portion \textbf{2B} and in the riser. Examples of polyolefin blends that can be obtained are:

- bimodal polyethylene blends containing the low molecular weight component in an amount higher than 70\% by wt;
- polypropylene blends containing a PP homopolymer in an amount lower than 30\% by wt and a PP random copolymer in an amount higher than 70\% by wt;
- heterophase propylene copolymers containing two copolymers of different ethylene content, wherein the amount of copolymer with the higher ethylene content is greater than 70\% by wt.

The above defined bimodal polyethylene blends obtained by means of the present invention are particularly suitable to be subjected to injection molding for preparing shaped articles.

The above defined heterophase propylene copolymers obtained by means of the present invention are particularly suitable for producing items endowed with a high balance of stiffness and impact resistance. These mechanical properties are particularly noteworthy in the automotive industry to produce interior trims and bumpers.

The polymerization process of the present invention can be carried out upstream or downstream other conventional polymerization technologies (either in a liquid-phase or a gas-phase) to give rise a sequential multistage polymerization process. For instance, a fluidised bed reactor can be used to prepare a first polymer component, which is successively fed to the gas-phase reactor of Fig. 1 to prepare a second and a third polymer component. Accordingly, an ethylene polymer endowed with a tri-modal molecular weight distribution can be obtained, as well as a polypropylene blend comprising three components having a different content in ethylene.

The polymerization process of the invention can be carried out in the presence of a highly active catalyst system of the Ziegler-Natta or metalloocene type.

A Ziegler-Natta catalyst system comprises the catalysts obtained by the reaction of a
transition metal compound of groups 4 to 10 of the Periodic Table of Elements (new notation) with an organometallic compound of group 1, 2, or 13 of the Periodic Table of element.

In particular, the transition metal compound can be selected among compounds of Ti, V, Zr, Cr, and Hf. Preferred compounds are those of formula Ti(OR)$_n$X$_{y-n}$ in which n is comprised between 0 and y; y is the valence of titanium; X is halogen and R is a hydrocarbon group having 1-10 carbon atoms or a COR group. Among them, particularly preferred are titanium compounds having at least one Ti-halogen bond such as titanium tetrahalides or halogenalcoholates. Preferred specific titanium compounds are TiCl$_4$, TiCl$_3$, Ti(OBu)$_4$, Ti(OBu)Cl$_3$, Ti(OBu)$_2$Cl$_2$, Ti(OBu)$_3$Cl.

Preferred organometallic compounds are the organo-Al compounds and in particular Al-alkyl compounds. The alkyl-Al compound is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as AlEt$_2$Cl and Al$_2$Et$_2$Cl$_3$ optionally in mixture with said trialkyl aluminum compounds.

Particularly suitable high yield ZN catalysts are those wherein the titanium compound is supported on magnesium halide in active form which is preferably MgCl$_2$ in active form. As internal electron donor compounds can be selected among esters, ethers, amines, and ketones. In particular, the use of compounds belonging to 1,3-diethers, phthalates, benzoates and succinates is preferred.

Further improvements can be obtained by using, in addition to the electron-donor present in the solid component, an electron-donor (external) added to the aluminum alkyl co-catalyst component or to the polymerization reactor. These external electron donor can be the same as, or different from, the internal donor. Preferably they are selected from alkoxy silanes of formula $R_a^1 R_b^2 Si(OR)^3$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; $R_a^1$, $R_b^2$, and $R_c^3$ are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms. Particularly preferred are the silicon compounds in which $a$ is 1, $b$ is 1, $c$ is 2, at least one of $R_a^1$ and $R_b^2$ is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and $R_c^3$ is a C$_{11}$-C$_{10}$ alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butylmethoxysilane, dicyclopentyldimethoxysilane. Moreover, are also preferred the silicon compounds in which $a$ is 0, $c$ is 3, $R_b^2$ is a branched alkyl or cycloalkyl group and $R_c^3$ is
methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and thexytrimethoxysilane.

The above cited catalysts show, in addition to a high polymerization activity, also good morphological properties that make them particularly suitable for the use in the gas-phase polymerization process of the invention.

Also metalloocene-based catalyst systems can be used in the process of the present invention and they comprise:

- at least a transition metal compound containing at least one π bond;
- at least an alumoxane or a compound able to form an alkylmetalloocene cation; and optionally an organo-aluminum compound.

A preferred class of metal compound containing at least one π bond are metalloocene compounds belonging to the following formula (I):

\[
\text{Cp}(L)_{n}AX_p
\]

(II)

wherein

- \(M\) is a transition metal belonging to group 4, 5 or to the lanthanide or actinide groups of the Periodic Table of the Elements; preferably \(M\) is zirconium, titanium or hafnium;
- the substituents \(X\), equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, \(R^6\), \(OR^6\), \(OCOR^6\), \(SR^6\), \(NR^6_2\) and \(PR^6_2\), wherein \(R^6\) is a hydrocarbon radical containing from 1 to 40 carbon atoms; preferably, the substituents \(X\) are selected from the group consisting of -Cl, -Br, -Me, -Et, -n-Bu, -sec-Bu, -Ph, -Bz, -CH₂SiMe₃, -OEt, -OPr, -OBu, -OBz and -NMe₂;
- \(p\) is an integer equal to the oxidation state of the metal \(M\) minus 2;
- \(n\) is 0 or 1; when \(n\) is 0 the bridge \(L\) is not present;
- \(L\) is a divalent hydrocarbon moiety containing from 1 to 40 carbon atoms, optionally containing up to 5 silicon atoms, bridging \(Cp\) and \(A\), preferably \(L\) is a divalent group \(\text{ZR}^7_2\); \(Z\) being C, Si, and the \(R^7\) groups, equal to or different from each other, being hydrogen or a hydrocarbon radical containing from 1 to 40 carbon atoms; more preferably \(L\) is selected from \(\text{Si(CH₃)}₂\), \(\text{SiPh₂}\), \(\text{SiPhMe}\), \(\text{SiMe(SiMe)}₃\), \(\text{CH₃}\), \(\text{(CH₂)}₂\), \(\text{(CH₃)}₂\) or \(\text{C(CH₃)}₂\);
- \(\text{Cp}\) is a substituted or unsubstituted cyclopentadienyl group, optionally condensed to one or more substituted or unsubstituted, saturated, unsaturated or aromatic rings;
- \(A\) has the same meaning of \(\text{Cp}\) or it is a \(\text{NR}^7\), -O, S moiety wherein \(R^7\) is a hydrocarbon radical containing from 1 to 40 carbon atoms;
Alumoxanes used as component b) are considered to be linear, branched or cyclic compounds containing at least one group of the type:

\[ \begin{array}{c}
  \text{U} \\
  \text{Al = O = Al} \\
  \text{U} \\
  \text{U}
\end{array} \]

wherein the substituents U, same or different, are defined above.

In particular, alumoxanes of the formula:

\[ \begin{array}{c}
  \text{U} \\
  \text{Al = O = (Al = O) \ n^1 = Al} \\
  \text{U} \\
  \text{U}
\end{array} \]

can be used in the case of linear compounds, wherein \( n^1 \) is 0 or an integer of from 1 to 40 and where the U substituents, same or different, are hydrogen atoms, halogen atoms, C\(_1\)-C\(_{20}\)-alkyl, C\(_3\)-C\(_{20}\)-cycalkyl, C\(_6\)-C\(_{20}\)-aryl, C\(_7\)-C\(_{20}\)-alkylaryl or C\(_7\)-C\(_{20}\)-aryllalkyl radicals, optionally containing silicon or germanium atoms, with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being also a non-integer number; or alumoxanes of the formula:

\[ \begin{array}{c}
  \text{U} \\
  \text{(Al = O) \ n^2} \\
  \text{U}
\end{array} \]

can be used in the case of cyclic compounds, wherein \( n^2 \) is an integer from 2 to 40 and the U substituents are defined as above.

The following examples will further illustrate the present invention without limiting its scope.

**EXAMPLES**

**Characterization**

Melt index L (MIL): ASTM-D 1238 (230°C/2.16 Kg)

Density: ASTM-D 792

Solubility index (X.S.): in xylene at 25°C

**Intrinsic viscosity of xylene soluble fraction:** in tetrahydronaphtalene at 135°C

Flexural elasticity modulus (MEF): ASTM D-790.

IZOD impact: ASTM D-4101

**Polydispersity index (PI):** this property is strictly connected with the molecular weight distribution of the polymer under examination. It is inversely proportional to the creep resistance of the polymer in molten state. Said resistance, called modulus separation at low
modulus value, i.e. 500 Pa, was determined at a temperature of 200°C by using a parallel plates rheometer model RMS-800 marketed by RHEOMETRICS (USA), operating at an oscillation frequency which increases from 0.1 rad/sec to 100 rad/sec. From the crossover modulus one can derive the P.I. by way of the equation:

$$P.I. = 10^{3}/G_c$$

in which $G_c$ is the crossover modulus which is defined as the value (expressed in Pa) at which $G' = G''$ wherein $G'$ is the storage modulus and $G''$ is the loss modulus.

**Example 1**

- **Preparation of a polypropylene blend** -

The process of the invention was carried out under continuous conditions in a plant comprising a reactor having interconnected polymerization zones, as shown in Figure 1.

The set of operative conditions allows preparing a propylene homopolymer in the portion 2A of the downcomer, while a random copolymer of propylene and ethylene is formed inside the riser and the portion 2B of the downcomer.

A Ziegler-Natta catalyst was used as the polymerization catalyst, comprising:

- a titanium solid catalyst component prepared with the procedure described in EP 728 769, Example 5, lines 46 to 53, according to which di-isobutyl phthalate is used as an internal donor compound;
- triethylaluminium (TEAL) as a cocatalyst;
- dicyclopentyl(dimethoxysilane as an external donor.

About 3 g/h of solid catalyst component are fed to a pre-contacting vessel, the weight ratio TEAL/solid component being of 7, the weight ratio TEAL/external donor being of 4. The above catalyst components are pre-contacted at a temperature of 15°C for 10 minutes.

The catalyst, after prepolymerization with propylene, was fed via line 12 to the gas-phase polymerization reactor of Figure 1. Propylene was polymerized using $H_2$ as the molecular weight regulator and in the presence of propane as inert diluent. The polymerization was carried out at a temperature of 80°C and at a pressure of 2.5 MPa.

Condition (a) as claimed in the process of the present invention was achieved by introducing a barrier fluid via line 18 into the upper part of the downcomer. The composition of said barrier fluid is given in Table 1.

Condition (b) as claimed in the process of the present invention was implemented by introducing a corrective fluid via line 21 into the downcomer. The composition of said
corrective fluid is given in Table 1.

The feeding of said corrective fluid via line 21 makes the gaseous composition in the portion 2B of the downcomer similar to the gaseous composition present in the riser. The compositions of the gas phases inside the riser 1 and inside the portions 2A and 2B of the downcomer are given in Table 2.

The obtained polypropylene blend is continuously discharged from the bottom of the downcomer via line 13. The properties of the obtained polymer composition were analyzed. As shown in Table 3, the polypropylene resin had a melt index MIL of 5.8, an ethylene content of 4.0% and a fraction soluble in xylene of 5.1% by weight.

The amount of polymer component prepared in the riser and in portion 2B was equal to 80% by weight with respect to the total blend.

**Example 2**

- **Preparation of a heterophasic propylene copolymer** -

A heterophasic propylene copolymer was produced by means of a sequence of two serially connected gas-phase reactors, each reactor having interconnected polymerization zones (riser and downcomer).

The same catalyst system of Example 1 was used. The catalyst together with propylene was fed to the first gas-phase reactor for producing a crystalline propylene homopolymer. The polymerization was carried out at a temperature of 75°C and at a pressure of 2.8 MPa. The first reactor produced about 72% by weight (split wt %) of the total amount of polymer produced by both first and second reactors. The propylene homopolymer obtained from the first reactor was continuously discharged, separated from the gas in a gas/solid separator, and introduced in the second gas-phase reactor having the configuration shown in Figure 1.

Said second gas-phase reactor was aimed at preparing an amorphous polymer fraction by copolymerizing ethylene with propylene. The second reactor was operated under polymerization conditions at a temperature of about 73 °C, and a pressure, of about 1.9 MPa.

The set of operative conditions in this second reactor allows preparing two ethylene/propylene copolymers having a different content of ethylene, the first copolymer being prepared in the portion 2A of the downcomer and the second one being prepared
inside the riser and the portion 2B of the downcomer.

Condition (a) as claimed in the process of the present invention was achieved by introducing a barrier fluid via line 18 into the upper part of the downcomer. The composition of said barrier fluid is given in Table 1.

Condition (b) as claimed in the process of the present invention was implemented by introducing a corrective fluid via line 21 into the downcomer. The composition of said corrective fluid is given in Table 1.

The feeding of said corrective fluid via line 21 makes the gaseous composition in the portion 2B of the downcomer similar to the gaseous composition present in the riser. The ethylene and propylene concentrations inside the riser 1 and inside the portions 2A and 2B of the downcomer are given in Table 2. The obtained heterophasic polypropylene copolymer is continuously discharged from the bottom of the downcomer via line 13.

The amount of copolymer prepared in the riser and in portion 2B was equal to 75% by weight with respect to the total blend.

Table 3 indicates the properties of the obtained heterophasic copolymer having a good balance of stiffness and impact resistance. The IZOD impact value at 23°C is of 10.5 kJ/m², while the flexural modulus is of 1007 MPa.

Example 3

- Preparation of a bimodal polyethylene blend -

The process of the invention was carried out under continuous conditions in a plant comprising a reactor having interconnected polymerization zones, as shown in Figure 1.

The set of operative conditions allows preparing a high molecular weight (HMW) polyethylene in the portion 2A of the downcomer and a low molecular weight (LMW) polyethylene inside the riser and the portion 2B of the downcomer.

A Ziegler-Natta catalyst was used as the polymerization catalyst, comprising:
- a titanium solid catalyst component prepared with the procedure described in WO 92/21706, Example 1, according to which diisobutyl phthalate is used as an internal donor compound;
- triethylaluminium (TEAL) as a cocatalyst;

About 6 g/h of solid catalyst component are fed to a pre-contacting vessel, the weight ratio
TEAL/solid component being of 6. The above catalyst components are pre-contacted at a temperature of 15°C for 10 minutes.

The catalyst, after prepolymerization with propylene, was fed via line 12 to the gas-phase polymerization reactor of Figure 1. Ethylene was polymerized using H₂ as the molecular weight regulator and in the presence of propane as inert diluent. The polymerization was carried out at a temperature of 80°C and at a pressure of 2.5 MPa.

Condition (a) as claimed in the process of the present invention was achieved by introducing a barrier fluid via line 18 into the upper part of the downcomer. The composition of said barrier fluid is given in Table 1.

Condition (b) as claimed in the process of the present invention was implemented by introducing a corrective fluid via line 21 into the downcomer. The composition of said corrective fluid is given in Table 1.

The compositions of the gas phases inside the riser 1 and inside the portions 2A and 2B of the downcomer are given in Table 2. The feeding of said corrective fluid via line 21 makes the gaseous composition in the portion 2B of the downcomer similar to the gaseous composition present in the riser, as witness by the comparable values of the ratios H₂/C₂H₄ and Ce/(Ce+C₂) in Table 2.

A polyethylene component having a low molecular weight and a low level of hexene modification was produced in the riser and 2B. A high molecular weight polyethylene component with a higher content of hexene was produced in 2A.

The obtained bimodal polyethylene blend is continuously discharged from the bottom of the downcomer via line 13.

The properties of the bimodal polyethylene produced in this way were measured, and are given in Table 3. The polyethylene resin had a melt index MIP of about 20 and a density of 0.955 g/cc.

The amount of polymer component prepared in the riser and in portion 2B was equal to 90% by weight.
## Table 1. Composition of the barrier and corrective fluid

<table>
<thead>
<tr>
<th></th>
<th>Example 1</th>
<th></th>
<th>Example 2</th>
<th></th>
<th>Example 3</th>
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<tbody>
<tr>
<td></td>
<td>Barrier</td>
<td>Corrective fluid</td>
<td>Barrier</td>
<td>Corrective fluid</td>
<td>Barrier</td>
<td>Corrective fluid</td>
</tr>
<tr>
<td>Propylene %mol</td>
<td>77</td>
<td>87.1</td>
<td>50.6</td>
<td>36.1</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Propane %mol</td>
<td>21</td>
<td>5.2</td>
<td>44.9</td>
<td>33.0</td>
<td>92.9</td>
<td>32.0</td>
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<tr>
<td>Ethylene %mol</td>
<td>-</td>
<td>4.6</td>
<td>0.1</td>
<td>28.4</td>
<td>6.38</td>
<td>50.4</td>
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<tr>
<td>Hydrogen %mol</td>
<td>2</td>
<td>3.1</td>
<td>4.3</td>
<td>2.5</td>
<td>0.13</td>
<td>17.6</td>
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<tr>
<td>Hexene %mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.61</td>
<td>-</td>
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<tr>
<td>(H_2/C_3H_6)</td>
<td>0.026</td>
<td>0.036</td>
<td>0.085</td>
<td>0.069</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(C_2H_6/(C_2H_4+C_3H_6))</td>
<td>0.000</td>
<td>0.050</td>
<td>0.002</td>
<td>0.440</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(H_2/C_2H_4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.020</td>
<td>0.349</td>
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<tr>
<td>(C_6/(C_8+C_2))</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.087</td>
<td>0.000</td>
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## Table 2. Composition of the gas phase in sections 1, 2A and 2B

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th>Example 3</th>
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<tbody>
<tr>
<td></td>
<td>Riser 1</td>
<td>Downer 2A</td>
<td>Downer 2B</td>
<td>Riser 1</td>
<td>Downer 2A</td>
<td>Downer 2B</td>
</tr>
<tr>
<td>Propylene %mol</td>
<td>76.8</td>
<td>77.1</td>
<td>75.0</td>
<td>36.4</td>
<td>55.4</td>
<td>36.2</td>
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<tr>
<td>Propane %mol</td>
<td>17.9</td>
<td>21.2</td>
<td>20.1</td>
<td>33.6</td>
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<td>35.3</td>
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<td>Ethylene %mol</td>
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<td>0.2</td>
<td>2.5</td>
<td>27.5</td>
<td>14.7</td>
<td>25.6</td>
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<tr>
<td>Hexene %mol</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen %mol</td>
<td>2.5</td>
<td>1.5</td>
<td>2.4</td>
<td>2.5</td>
<td>4.6</td>
<td>2.9</td>
</tr>
<tr>
<td>(H_2/C_3H_6)</td>
<td>0.033</td>
<td>0.019</td>
<td>0.032</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(C_2H_6/(C_2H_4+C_3H_6))</td>
<td>0.035</td>
<td>0.003</td>
<td>0.032</td>
<td>0.43</td>
<td>0.21</td>
<td>0.41</td>
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<tr>
<td>(H_2/C_2H_4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.069</td>
<td>0.083</td>
<td>0.080</td>
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<tr>
<td>(C_6/(C_8+C_2))</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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### Table 3. Physical/Mechanical Properties of the products

<table>
<thead>
<tr>
<th></th>
<th>Example 1</th>
<th></th>
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<th>Ex. 3</th>
<th>Final</th>
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<tr>
<td></td>
<td>1</td>
<td>2A</td>
<td>2B</td>
<td>Final</td>
<td>1</td>
<td>2A</td>
<td>2B</td>
<td>Final</td>
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<td>5.5</td>
<td>5.7</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15.4</td>
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<tr>
<td>Xylene solubles</td>
<td>6.0</td>
<td>1.5</td>
<td>5.8</td>
<td>5.1</td>
<td>79.7</td>
<td>91.9</td>
<td>82.9</td>
<td>20.4</td>
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<tr>
<td>C2 content</td>
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<td>4.9</td>
<td>4.0</td>
<td>56.2</td>
<td>37.0</td>
<td>53.4</td>
<td>13.5</td>
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<td>IVXS</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.87</td>
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<tr>
<td>IZOD @ 25°C</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.5</td>
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<tr>
<td>Flex. Mod.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1007</td>
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<tr>
<td>Melt Flow Rate P</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
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<tr>
<td>Density</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.955</td>
</tr>
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CLAIMS

1. A process for the gas-phase polymerization of $\alpha$-olefins $\text{CH}_2=\text{CHR}$, where R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, carried out in a first and a second interconnected polymerization zones, to which one or more of said $\alpha$-olefins are fed in the presence of a catalyst under reaction conditions and from which the polymer product is discharged, wherein the growing polymer particles flow through the first of said polymerization zones (riser) under fast fluidization conditions, leave said riser and enter the second of said polymerization zones (downcomer) through which they flow downward in a densified form, leave said downcomer and are reintroduced into said riser, in which process:

(a) the gas mixture present in the riser is totally or partially prevented from entering the downcomer, and

(b) the gaseous composition inside a portion of the downcomer is maintained substantially similar to the gaseous composition reacting in the riser.

2. The process according to claim 1, wherein said condition (a) is achieved by introducing into the upper part of said downcomer a gas and/or liquid mixture having a composition different from the gaseous mixture present in the riser.

3. The process according to any of claims 1-2, wherein said condition (b) is implemented by feeding a fluid of a suitable composition ("corrective fluid") in correspondence of the upper level of said portion of the downcomer.

4. The process according to claim 3, wherein said corrective fluid is a gaseous mixture or a gas/liquid mixture.

5. The process according to any of claims 1-4, wherein the mutual mixing between said corrective fluid and the gas flowing downwardly in the downcomer is such to satisfy said condition (b).

6. The process according to any of claims 1-5, wherein the split of one of the two (co)polymer components prepared by means of said polymerization process is adjusted by rising or lowering along said downcomer the feeding point of said corrective fluid.

7. The process according to any of claims 1-6, wherein said corrective fluid comes from the recycle gas stream.

8. The process according to any of claims 1-7, wherein said corrective fluid contains,
besides the monomers to be polymerized, also condensable inert compounds.

9. The process according to any of claims 1-8, wherein the composition of said corrective fluid is adjusted by feeding make-up monomers, polymerization diluents, and hydrogen before its introduction into the downcomer.

10. The polymerization process according to any of claims 1-9, where said process is upstream or downstream other conventional polymerization technologies (either in a liquid-phase or a gas-phase) in a sequential multistage polymerization process.
# INTERNATIONAL SEARCH REPORT

**International application No**

PCT/EP2006/062148

## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, IBM-TDB

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<td>WO 2006/067052 A (BASELL POLIOLEFINE ITALIA S.R.L.; MEI, GABRIELE; PATER, JOACHIM; BERTOL) 29 June 2006 (2006-06-29) the whole document</td>
<td>1-10</td>
</tr>
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* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other reasons
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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "8" document member of the same patent family

Date of the actual completion of the international search: 25 July 2006

Date of mailing of the international search report: 01/08/2006

Name and mailing address of the ISA/

European Patent Office, P.B. 5318 Patentlaan 2 NL - 5202 HV Rijswijk

Tel. (+31-70) 346-2040, Tx. 31 651 epo nl, Fax: (+31-70) 940-3016

Authorized officer: Gold, J
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