Title: PROCESS FOR PRODUCING POLYPROPYLENE

Abstract: The invention concerns a process for producing propylene, and polypropylenes produced thereby. According to the process, propylene is homo- or copolymerized in a reaction sequence including at least one bulk reaction zone and at least one gas phase reaction zone arranged in series. The polymerization is carried out in the presence of a Ziegler-Natta type catalyst system including a catalyst component, a cocatalyst component and an external donor. According to the invention the catalyst component, the external donor and a part of the cocatalyst component are fed to a first reaction zone, and the rest of said cocatalyst component is fed to a second reaction zone.
PROCESS FOR PRODUCING POLYPROPYLENE

Background of the Invention

Field of the Invention

The present invention relates to propylene polymerization. In particular, the present invention concerns a process for producing homo- or random copolymers of propylene in the presence of a Ziegler-Natta type catalyst in a process comprising a combination of at least one bulk reactor and at least one gas phase reactor.

Description of Related Art

A large number of processes for producing propylene homo- and copolymers are known in the art. Previously, slurry or gas phase processes were used, but nowadays polypropylene appears to be produced with a process in which the polymerization is carried out in a reactor sequence comprising both slurry or bulk and gas phase reactors. Catalysts used in these processes comprise for example Ziegler-Natta type catalysts which typically are used together with a cocatalyst and an external donor.

The polymerization is preferably carried out in a process comprising both bulk, e.g., loop and gas phase reactors, usually in that order. The melt flow rate (MFR) of the fraction of the final product produced in bulk reactor is typically same as or lower than the MFR of the fraction produced in the gas phase reactor (depending on whether unimodal or multimodal polymer is produced). The higher MFR is obtained by means of feeding hydrogen and/or ethylene into the gas phase reactor. The final product can then exhibit a narrow or broad molecular weight distribution (MWD). Usually better processing properties of the polymer material are achieved with a broader MWD. In this kind of a process an external donor is used to get a stiff matrix with a low amount of xylene solubles (XS).

As is obvious, the broadness of the molecular weight distribution of the final product depends on percentages of the fractions with different MFRs. Since a specific combination of the fractions is required in the end product, a split is also required in the production. In
other words, a certain percentage of the material has to be produced in the loop reactor and a certain fraction in the gas phase reactor in order to obtain a desired final product.

Conventionally, the catalyst together with cocatalyst and the external donor are fed (optionally via prepolymerization) to the first reactor in the reactor sequence, which is typically a bulk reactor, e.g., a loop reactor. The problem with the processes of the prior art is that the lifetime of the catalyst is, however, restricted. A high excess of the amount of the cocatalyst with regard to what is needed for activating the catalyst in the loop reactor creates a high activity in the loop reactor, and when the material enters to the gas phase reactor, the activity of the catalyst drops. This is due to the conditions in the gas phase reactor and the fact that a great portion of the catalyst activity has been used in the loop reactor. Thus, in the gas phase reactor, the catalyst is already partly deactivated, and the deactivation process is still going on.

Since this kind of a catalyst feed creates a high activity in the loop reactor, the residence time in the loop is typically short. On the other hand, since the catalyst activity in the gas phase reactor is low, long residence times are required in order to achieve an end product with desired properties. The reactivity of the catalyst in the gas phase reactor has typically been 2 to 5 times poorer compared with the reactivity in the bulk polymerization. This will lead to the gas phase reactor becoming a capacity bottle neck in the polymerization process.

Further, it has been noted that if an excess of cocatalyst is fed to the loop reactor, it is very usual that formation of oligomers occurs, which results in undesired odour and taste of the products. In addition, aluminium oxides are formed, which lead to blocking problems in the filters of the monomer circulating compressors.

**Summary of the Invention**

It is an object of the present invention to eliminate the problems of the prior art and to provide a novel process for producing both uni- and multimodal propylene homo- and random copolymers.
This and other objects, together with the advantages thereof over known processes, which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

According to the present invention propylene is homo- or copolymerized in a process comprising a combination of at least one bulk reaction zone including at least one bulk reactor and at least one gas phase reaction zone including at least one gas phase reactor. Polymerization is thus carried out in at least two subsequent polymerization reactors in the presence of a Ziegler-Natta type catalyst including a catalyst component, a cocatalyst component and an external donor.

Preferably, the first reaction zone is a bulk polymerization zone and the second reaction zone is a gas phase polymerization zone. The reactors are preferably arranged in series.

The present invention is based on the idea that, in order to improve the catalyst activity in the second reaction zone, the feed of the cocatalyst is split between the bulk polymerization zone and the gas phase polymerization zone. Only a fraction of the cocatalyst is fed into the first polymerization zone, together with an excess amount of external donor which blocks the catalyst to a certain amount. This leads to a slower reactivity of the catalyst in the first polymerization zone, since the Ti$^{4+}$ in the catalyst component is only partly reduced to Ti$^{3+}$ (I). The rest of the cocatalyst component is fed to the second polymerization zone. This increases the activity of the catalyst in the second polymerization, since fresh Ti$^{3+}$ which is not deactivated at all, is formed (II). Thus an equal productivity in both of the polymerization zones is achieved.

\[
\begin{align*}
2 \text{Ti}^{4+} - \text{MgCat} + \text{TEA} &= \text{Ti}^{3+} + \text{Ti}^{4+} - \text{MgCat} + \text{Cat}' \quad (I) \\
\text{Ti}^{3+} + \text{Ti}^{4+} - \text{MgCat} + \text{TEA} &= 2 \text{Ti}^{3+} - \text{MgCat} + \text{Cat}' \quad (II)
\end{align*}
\]

In the above formulas (I) and (II), Cat' designates the deactivated catalyst.

More specifically, the process according to the present invention is characterised by what is stated in the characterising part of claim 1.
The bimodal propylene polymer, being one embodiment of the present invention is characterised by what is stated in the characterising part of claim 18.

A number of considerable advantages are achieved by means of the invention. As described above, the typical way to operate a process for producing propylene homo- or random copolymers is to arrange the loop reactor before the gas phase reactor and to feed the whole catalyst composition to the loop reactor. According to the present invention, when the cocatalyst feed is split, the activity of the catalyst in the gas phase reaction zone is considerably higher and thus the residence times in the gas phase reaction zone are shorter than in the processes of the prior art. This results in a faster process and thus increases the polymer production, or allows for decreasing of the size of the gas phase reactor, which decreases the investment costs. Generally, residence times according to the present invention can be 60 - 70 % of the residence times required previously.

With the aid of the invention the reactivity of the catalyst in the gas phase reactor(s) and the lifetime of the catalyst are improved and thus it is possible to operate in even, e.g., three gas phase reactors in series after the bulk polymerization. This is important in view of the often desired modification of the polymer properties in additional gas phase reactors, in order to obtain, e.g., elastic properties for the material.

By means of the present invention the production split can be controlled efficiently. In prior art processes the split has been adjusted by pressure and surface level of the gas phase reactor, which is slow. Also grade changes can be made faster by using the process of the present invention.

The polypropylene material produced according to the present process can be made extremely isotactic even with a remote amount of donor. This is possible since, with the process of the present invention, the amount of donor in proportion to cocatalyst is high in the loop reactor (presuming loop reactor is the first reactor in series). Generally, more isotactic material can be produced in a gas phase reactor, and thus, after the gas phase reaction zone, an extremely isotactic and stiff material is obtained.

Further, the present invention contributes to better odour and taste properties of the polymers, which is due to the fact that less alkyl is needed in the first polymerization stage, e.g., in loop reactor, and thus less oligomers are formed.
In addition, blocking problems in filters can be avoided due to the decrease in formation of aluminium oxides.

5 **Detailed Description of the Invention**

**Definitions**

In the field of polymerization, "slurry reactor" designates any reactor, such as a continuous or simple batch stirred tank reactor or loop reactor, operating in bulk or slurry and in which the polymer forms in particulate form. "Bulk" means a polymerization in reaction medium that comprises at least 60 wt-% monomer. A bulk reactor is used in the process of the present invention. According to a preferred embodiment the bulk reactor comprises a loop reactor.

10 By "gas phase reactor" is meant any mechanically mixed or fluid bed reactor. Preferably the gas phase reactor comprises a mechanically agitated fluidized bed reactor with gas velocities of at least 0.2 m/sec.

"Reaction zone" or "polymerization zone" stands for one or several reactors of similar type producing the same type or characteristics of polymer connected in the series.

By "catalyst" or "catalyst system" is meant a system comprising a catalyst component, a cocatalyst component, an external donor and, optionally, an internal donor.

20 "First cocatalyst feed" designates the feed of the cocatalyst to the prepolymerization stage or to the first reaction zone, while "second cocatalyst feed" designates the feed of the cocatalyst to the second reaction zone.

**The catalyst**

The catalyst system used in the present process is preferably a propylene stereospecific, high yield Ziegler-Natta catalyst capable of polymerising propylene at reaction conditions. Generally, the Ziegler-Natta catalyst system used in the present invention comprises a catalyst component, a cocatalyst component and an external electron donor.
Suitable catalyst systems are described in, for example, in US 5 234 879, EP 627 449, WO 92/19653 and WO 92/19658. Of these, the catalyst disclosed in WO 92/19653 is particularly preferred.

The catalyst component

The catalyst component contains primarily a procatalyst component containing typically magnesium, titanium, halogen, and an internal electron donor.

A catalyst component useful in the present process can be prepared by reacting a magnesium halide compound with a titanium compound, preferably titanium tri- or tetrachloride, and an internal donor. Also other transition metal compounds, such as vanadium, zirconium, chromium, molybdenum and tungsten compounds can be mixed with the titanium compound. The magnesium halide compound is, for example, selected from the group of magnesium chloride, a complex of magnesium chloride with lower alcohol and other derivatives of magnesium chloride. MgCl₂ can be used as such or it can be combined with silica, e.g. by filling pores of the silica with a solution or slurry containing MgCl₂. The lower alcohol used can be preferably methanol or ethanol, particularly ethanol.

One particularly attractive catalyst type comprises a transesterified catalyst, in particular a catalyst transesterified with phthalic acid or its derivatives (cf. Finnish Patent No. 88047). The alkoxy group of the phthalic acid ester used in the transesterified catalyst comprises at least five carbon atoms, preferably at least 8 carbon atoms. Thus, as the ester can be used for example propylhexyl phthalate, dioctyl phthalate, dinonyl phthalate, diisodecyl phthalate, di-undecyl phthalate, ditridecyl phthalate or ditetradecyl phthalate.

The partial or complete transesterification of the phthalic acid ester can be carried out e.g. by selecting a phthalic acid ester - a lower alcohol pair, which spontaneously or with the aid of a catalyst, which does not damage the procatalyst composition, transesterifies the catalyst at an elevated temperatures. It is preferable to carry out the transesterification at a temperature, which lies in the range of 110 to 150 °C, preferably 120 to 140 °C.
The external donor

The external donor is a compound added to the reactor in order to increase the stereoselectivity of the catalyst. The external donor used in the process of the present invention is, for example, a silane based donor having generally the formula (III), or a 1,3-diether donor having the formula (IV).

\[ R_nR'_{(n-m)}Si(O)_{4-n-m} \]  

(III)

wherein

R and R' can be the same or different and they stand for a linear, branched or cyclic aliphatic, or aromatic group;

R'' is methyl or ethyl;

n is an integer 0 to 3;

m is an integer 0 to 3; and

n+m is 1 to 3.

\[ R'RR''_{C(COMe)}_2 \]  

(IV)

wherein R' and R'' are the same or different and stand for a linear, branched or cyclic aliphatic or aromatic group.

The groups R and R', when being aliphatic, can be saturated or unsaturated. Linear C_1 to C_{12} hydrocarbons include methyl, ethyl, propyl, butyl, octyl and decanyl. As examples of suitable saturated branched C_{1-8} alkyl groups, the following can be mentioned: isopropyl, isobutyl, isopentyl, tert-butyl, tert-amyl and neopentyl. Cyclic aliphatic groups containing 4 to 8 carbon atoms comprise, e.g., cyclopentyl, cyclohexyl, methyl cyclopentyl and cycloheptyl.

Typically the donors used in the process of the present invention are strongly co-ordinating donors which form relatively strong complexes with catalyst surface, mainly with MgCl_2 surface in the presence of aluminium alkyl and TiCl_4. The donor components are characterised by a strong complexation affinity towards catalyst surface and a sterically large and protective hydrocarbon. Strong co-ordination with MgCl_2 requires oxygen-oxygen distance of 2.5 to 2.9 Å [Albizzati et al., Macromol. Symp. 89 (1995) 73-89].
Typically this kind of donors have the structure of the general formula (V)

\[ R''_{n} \text{Si(OMe)}_{4-n} \]  

(V)

wherein \( R'' \) is a branched aliphatic or cyclic or aromatic group, and \( n \) is 1 or 2, preferably.


In particular, the external donor is selected from the group consisting of dicyclopentyl dimethoxysilane, diisopropyl dimethoxysilane, methylcyclohexyl dimethoxysilane, di-isobutyl dimethoxysilane, and di-t-butyl dimethoxysilane, dicyclopentyl dimethoxysilane being particularly preferred.

**The cocatalyst component**

The cocatalyst component is selected from the group of organometallic compounds. Typically, the cocatalysts are metal hydrides, or alkyls or aryls of metals. The metal is typically aluminium, lithium, zinc, tin cadmium, beryllium or magnesium. Especially preferred cocatalyst is organoaluminium compound, in particular trialkyl aluminium, dialkyl aluminium chloride or alkyl aluminium sesquichloride. According to a preferred embodiment, the cocatalyst is triethyl aluminium (TEA).

**The overall process**

The present invention concerns a multistage process consisting of at least one bulk reaction zone including at least one bulk reactor, and at least one gas phase reaction zone including at least one gas phase reactor. Typically, the at least one bulk reaction zone is arranged before the gas phase reaction zone, when the gas phase reaction zone is arranged in a cascade with at least one bulk reactor with a feed to the gas phase for homo- or random copolymerizing propylene.

In the following, the reaction system comprises at least one bulk reaction zone (referred to as “the first reaction zone”) and at least one gas phase reaction zone (referred to as “the second reaction zone”), in that order, which is a preferred process configuration for making homo- or random copolymer of propylene, and especially bimodal polypropylene.
However, it should be understood that the reactor system can comprise the reaction zones in any number and order. Each of the reaction zones can, and typically do, contain more than one reactor. The most typical process configuration comprises one bulk reactor, which preferably is a loop reactor, and one gas phase reactor. Still, combinations like two bulk reactors and one gas phase reactor or one bulk reactor and two or more gas phase reactors, connected in series in any order, are also possible.

The high MFR portion and the low MFR portion of the product can be prepared in any order in the reactors. A separation stage can be employed between the reactors to prevent the carryover of reactants from the first polymerization stage into the second one.

In addition to the actual polymerization reactors used for producing the propylene homo- or random copolymer, the polymerization reaction system can also include a number of additional reactors, such as pre- and/or postreactors. The prereactors include any reactor for prepolymerizing the catalyst with propylene and/or other \(\alpha\)-olefin(s) and/or ethylene, if necessary. The postreactors include reactors used for modifying and improving the properties of the polymer product. A typical example are additional gas phase reactors for obtaining elastic properties. All reactors of the reactor system are preferably arranged in series.

Thus, according to the invention, the polymerization process comprises at least the following steps of

- subjecting propylene and optionally comonomer(s) and/or hydrogen to polymerization or copolymerization in a first reaction zone or reactor,
- feeding catalyst component, external donor and a part of the cocatalyst component to the first reaction zone,
- transferring the polymerization product of the first reaction zone or reactor with the reaction medium into a second reaction zone or reactor and optionally feeding comonomer(s) and/or hydrogen and/or additional propylene into the second reaction zone or reactor,
- feeding rest of the cocatalyst component to the second reaction zone,
- continuing the polymerization reaction in the second reaction zone in the presence of the first polymerization product to produce a combined polymerization product, and
– separating and recovering the final polypropylene product from the second reaction product.

The comonomer(s) optionally used in any or every reactor are preferably C₂ to C₁₀ olefins, e.g. ethylene, 1-butene, 4-methyl-1-pentene, 1-hexene, dienes, or cyclic olefins, or a mixture thereof. Different amounts of hydrogen can be used as a molar mass modifier or regulator in any or every reactor.

The polymerization is carried out in the presence of a catalyst described above. The catalyst is fed to the process in at least two stages, so that the catalyst component and the external donor, and a part of the total amount of the cocatalyst component is fed to the first reaction zone to the first reactor in series. Additionally, the rest of the total amount of the cocatalyst component is fed to the second reaction zone, preferably to the first reactor of the second reaction zone.

The first reaction zone in series can optionally include also a prepolymerization stage. The catalyst is then subjected to prepolymerization prior to feeding into the first actual polymerization reactor of the reaction zone. During prepolymerization the catalyst components are contacted with a monomer, such as an olefin monomer or a mixture of monomers, before feeding into the first actual polymerization reactor. The monomer used in the prepolymerization is typically, but not necessarily the same as in the actual polymerization reactions. Examples of suitable systems are described in, for example, WO 97/33920.

It is also possible to carry out the prepolymerization in the presence of a viscous substance, such as an olefinic wax, to provide a prepolymerized catalyst which is stable during storage and handling. The catalyst prepolymerized in wax will allow for easy dosing of the catalyst into the polymerization reactors. Examples of suitable systems are described in, for example, EP 607 703.

If the catalyst is prepolymerized, then preferably also the first feed of the cocatalyst is conducted to the prepolymerization. According to a typical embodiment, the catalyst is flushed to the prepolymerization reactor with a monomer (e.g., propylene) and also the donor and part of the cocatalyst component are fed to the reactor.
The split of the cocatalyst component feed varies. Typically 10 to 40 wt-\%, preferably 20 to 30 wt-\%, of the total cocatalyst component feed is fed to the first reaction zone, or to the prepolymerization stage optionally included in it, and 90 to 60 wt-\%, preferably 80 to 70 wt-\% of the total cocatalyst component feed is fed to the second reaction zone.

According to a preferred embodiment, the reactor sequence comprises at least one prepolymerization reactor, at least one bulk reactor, and at least one gas phase reactor, connected in series, in that order. In this kind of arrangement, the first feed of the cocatalyst is advantageously conducted to the prepolymerization reactor(s), and the rest of the cocatalyst is fed to the gas phase polymerization reactor(s).

The molar ratio of aluminium in the cocatalyst component to titanium (Al/Ti) in the catalyst component in the first feed of the cocatalyst is 10 – 150, preferably 30 – 100 and in particular 40 – 80. The total molar ratio of aluminium to titanium (the first and the second feed of the cocatalyst together) is 200 – 500, preferably 200 – 350 and in particular 250 – 300.

The molar ratio of aluminium in the cocatalyst component to donor (Al/D) in the first feed of the cocatalyst is 1 – 10, preferably 1 – 5 and in particular 2 – 3. The total molar ratio of aluminium to donor (the first and the second feed of the cocatalyst together) is 5 – 100, preferably 10 – 50 and in particular 10 – 30.

From the prepolymerization, the prepolymerized slurry is conducted to the first reaction zone. If no prepolymerization is carried out, then the catalyst component and the external donor and part of the cocatalyst component are fed directly to the first reaction zone. Propylene and optionally copolymers are also fed to the first reaction zone.

The first reaction zone is preferably a bulk polymerization zone. Bulk polymerization is carried out in a reaction medium, such as propene. The bulk polymerization is preferably carried out in a loop reactor.

The temperature in the loop is typically in the range of 40 to 110 °C, preferably in the range of 50 to 100 °C, and even more preferably for homopolymers 80 to 100 °C and for
copolymers of high comonomer content 60 to 75 °C and for copolymer with high comonomer randomness 75 to 85 °C. The reaction pressure is in range of 30 to 100 bar, preferably 35 to 80 bar.

In bulk polymerization zone more than one reactor can be used in series. In such a case the polymer suspension is fed without separation of inert components and monomers intermittently or continuously to the following bulk reactor.

The polymerization heat is removed by cooling the reactor with a cooling jacket. The residence time in the bulk polymerization zone depends on the catalyst activity and on the desired composition of the end products. Generally, the residence time in a bulk reactor must be at least 10 minutes, preferably 20-100 min for obtaining a sufficient degree of polymerization. A typical residence time is between 40 and 60 min.

The content of the bulk reactor, the polymerization product and reaction medium together with unreacted monomer and the catalyst, can be led directly to the second reaction zone, typically to a fluidized bed gas phase reactor. Alternatively, some components, e.g. hydrogen, can fully or partially be removed with various technical solutions before the flow enters the second reaction zone.

The second cocatalyst feed is preferably directed to the material flow of the first reactor to the second reaction zone. Alternatively, the second cocatalyst feed can be introduced separately to the first reactor in the second reaction zone. When there are more than one reactor operating in the second reaction zone, the second cocatalyst feed can be divided so that some fresh cocatalyst is fed to each of the reactors in the reaction zone. It is also possible to feed rest of the cocatalyst to part of the reactors in the second reaction zone.

The second reaction zone is preferably a gas phase reaction zone including at least one gas phase reactor, wherein propylene and optionally comonomer(s) are polymerized in a reaction medium comprising gas or vapour.

The gas phase reactor can be an ordinary fluidized bed reactor, although other types of gas phase reactors can be used. The bed of the fluidized bed reactor consists of the formed and growing polymer particles and of the still active catalyst, which has come along with
the polymer fraction from the bulk reactor. The bed is kept in a fluidized state by
introducing gaseous components, e.g. monomer on such flow rate (at least 0.2 m/s) which
make the particles act as a fluid. The fluidizing gas can contain also inert carrier gases, like
nitrogen and also hydrogen as a molecular weight modifier.

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The gas phase reactor used can be operated in the temperature range of 50 to 115 °C,
preferably between 60 and 110 °C and reaction pressure between 10 and 40 bar and below
the dew point. The partial pressure of the monomer between 2 and 30 bar or more.

10 Fresh propylene is preferably, but not necessarily fed to the gas phase polymerization zone.
Optionally, also comonomer(s) are fed to the gas phase polymerization zone.

The residence time in the gas phase polymerization zone depends on the activity of the
catalyst and on the desired composition of the end product. Since the catalyst activity in the
second reaction zone is improved by means of the present invention, the residence times
are generally shorter than in the prior art processes. A typical residence time in a gas phase
reactor is, according to the present invention, typically 1 – 2.5 h, preferably 1.5 – 2.2 h.

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The pressure of the second polymerization product including the gaseous reaction medium
is then reduced after the first gas phase reactor in order to separate part of the gaseous and
possible volatile components (e.g. heavy comonomers and compounds used for catalyst
feeds) of the product e.g. in a flash tank. The overhead stream or part of can be circulated
to the first gas phase reactor or to the bulk polymerization zone.

20 If desired, the polymerization product can be fed into additional gas phase reactor(s) to
produce a modified polymerization product having, e.g., elastomeric properties, from
which the polypropylene is separated and recovered. The present invention facilitates this
kind of production, since the high reactivity of the catalyst in the gas phase reaction zone
enables the use of even three gas phase reactors in series with a reasonable production rate.

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The production split between the bulk polymerization zone and the gas phase
polymerization zone is 5 - 95 : 95 - 5, preferably 20 – 80 : 80 – 20 and in particular 40 –
60 : 60 – 40. Thus, preferably, 5 to 60 %, in particular 20 to 60 %, of the propylene
homopolymer or random copolymer is produced at conditions to provide the polymer
fraction having a relatively high molecular weight and thus relatively low MFR₂, and 95 to 40 %, in particular 80 to 40 %, of the propylene homopolymer or random copolymer is produced at such conditions that provide a polymer with a higher MFR₂.

The present process is advantageously used for producing polypropylenes with a wide range of MFR₂ values, i.e., MFR₂ is in the range of 0.01 – 2000 g/10 min, preferably in 0.1 – 1000 g/10 min and in particular 1 – 400 g/10 min.

The xylene solubles fraction (XS) of the polymer material is typically 1.5 to 5 wt-%, in particular 1.8 - 3 wt-%.

According to one special embodiment of the invention, bimodal polypropylene is produced in order to obtain a material with a broad MWD and thus also an enhanced processability. As an example, the MFR₂ of the low molecular weight fraction of the bimodal polymer is approximately 50 g/10 min, and the MFR₂ of the high molecular weight fraction is approximately 2 g/10 min or less, and in particular 0.01 – 1.6 g/10 min. The xylene soluble fraction of the bimodal homopolymer material is typically for such polymers less than 1.8 wt-%, preferably less than 1.6 wt-%.

**Description of Analytical Methods**

**MFR:** The melt flow rate of the polymer material was determined according to ISO standard 1133 using a piston load of 2.16 kg and a temperature of 230 °C. The abbreviation “MFR“ is generally provided with a numerical subindex indicating the load of the piston in the test. Thus, e.g., MFR₂ designates a 2.16 kg load.

**Xylene Solubles (XS):** Determination of xylene soluble fraction (XS): 2.0 g of polymer is dissolved in 250 ml p-xylene at 135 °C under agitation. After 30±2 minutes the solution is allowed to cool for 15 minutes at ambient temperature and then allowed to settle for 30 minutes at 25±0.5 °C. The solution is filtered with filter paper into two 100 ml flasks.

The solution from the first 100 ml vessel is evaporated in nitrogen flow and the residue is dried under vacuum at 90 °C until constant weight is reached.
The xylene soluble fraction is calculated using the following equation:

\[
\text{XS \%} = \frac{(100 \times m_1 \times v_0)}{(m_0 \times v_1)},
\]

wherein

- \(m_0\), initial polymer amount (g)
- \(m_1\), weight of residue (g)
- \(v_0\), initial volume (ml)
- \(v_1\), volume of analysed sample (ml).

**Example 1**

In this example, a homopolymer with a broad MWD for moulding applications was produced.

**Catalyst**

A highly active propylene polymerization catalyst of ZN type, prepared according to WO 92/19653, was used.

**Catalyst feed, prepolymerization, polymerization in loop reactor**

Mixture of the catalyst and viscous medium was fed with non valve piston pump according to Finnish Patent No. 94164. The catalyst was contacted with triethyl aluminium (TEA) and dicyclopentyl dimethoxysilane (donor D) in pipeline. Al/Ti molar ratio was 80 (mol/mol) and Al/D molar ratio was 3. The activation time between catalyst, cocatalyst and donor was 15 seconds before these chemicals were fed to polymerization.

The catalyst was flushed with propylene to the prepolymerization reactor (CCSTR = Compartmented Continuous Stirred Tank Reactor) in which also TEA and D-donor were fed. The CCSTR has been described in WO 97/33920. The residence time of the particles was 8 – 10 minutes. Hydrogen feed to the prepolymerization reactor was 0.1..0.2 mol-%. The prepolymerized catalyst component was used in a loop reactor and a gas phase reactor connected in series.

The operating temperature in the loop reactor was 80 °C and the pressure was 55 bar. The residence time in the loop reactor was 0.75 h.

The MFR₂ (measured according to ISO 1133, with a load of 2.16 kg and a temperature of 230 °C) was set to be 1.5 – 2 by adjusting the hydrogen feed accordingly. The isotacticity
was kept as high as possible by adjusting the donor feed accordingly, and at the same time, the xylene solubles (XS) values were kept as low as possible.

Direct feed line between the loop and the gas phase reactor (GPR) and polymerization in the GPR

Direct feed line was used between loop and GPR. The rest of TEA (the total molar ratio of Al/Ti was 300) was fed to material stream between the loop reactor and the GPR.

The gas phase reactor was operated at 80 °C and 29 bar total pressure. The production split between the loop reactor and the gas phase reactor was about 40/60. The residence time in the GPR was 2.1 h.

The MFR₂ (2.16 kg / 230 °C) of the final product was set to be about 20 by adjusting the hydrogen feed accordingly.

Polymerization conditions and a main product analysis are shown in Table 1.

Comparative Example 1

The polymerization was carried out as in Example 1, except that the TEA split was not used. Al/Ti molar ratio to the catalyst contacting stage was 250 and Al/D molar ratio was 10. The greater amount of TEA fed in the catalyst contacting stage created a higher catalyst activity in the loop reactor. The activity of the catalyst dropped when it entered the gas phase reactor. The drop in activity was due to the conditions in the GPR and the fact that a great deal of the catalyst activity had already been used in the loop reactor. The catalyst has a restricted living time, and thus also the deactivation of the catalyst was going on.

The reactivity of the catalyst was not so good in the GPR. The production split turned from 40/60 to 60/40 despite the fact that the residence time in the GPR was longer (3.0 h).

In addition, the XS value was not on such a level as in Example 1. Further, the molecular weight distribution of the final material (measured with MFR₂) was not as broad by using the same amounts of hydrogen as in Example 1.

The polymerization conditions and a main product analysis are shown in Table 1.
Example 2

The polymerization was carried out as in Example 1, except that the molar ratio Al/Ti in the catalyst contacting stage was only 50 and the Al/D ratio was 2. Compared to Example 1 even a higher catalyst activity in the GPR was reached, which can be seen accordingly in a shorter residence time in the GPR. Also the isotactity (XS) of the product was better.

Polymerization conditions and a main product analysis are presented in Table 1.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Example 1</th>
<th>Comparative</th>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>ZN-type</td>
<td>ZN-type</td>
<td>ZN-type</td>
</tr>
<tr>
<td>Catalyst feed</td>
<td>g/h</td>
<td>0.60</td>
<td>0.45</td>
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<tr>
<td>TEA split in use</td>
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<td>NO</td>
<td>YES</td>
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<tr>
<td>Al/Ti to prepolymerization</td>
<td>mol/mol</td>
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<td>250</td>
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<td>Al/D to prepolymerization</td>
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Claims:

1. A process for producing homo- and random copolymers of propylene in at least two reaction zones, comprising
   - polymerizing propylene, optionally together with hydrogen and/or comonomers, in a reaction sequence including at least one bulk reaction zone and at least one gas phase reaction zone arranged in series, in the presence of a Ziegler-Natta type catalyst system including a catalyst component, a cocatalyst component and an external donor,
   - feeding said catalyst component, said external donor and a part of the total amount of said cocatalyst component to a first reaction zone, and
   - feeding the rest of said cocatalyst component to a second reaction zone.

2. The process according to claim 1, wherein the first reaction zone is a bulk polymerization zone comprising at least one bulk reactor, and the second reaction zone is a gas phase polymerization zone comprising at least one gas phase reactor.

3. The process according to claim 1 or 2, wherein the first reaction zone comprises a prepolymerization stage.

4. The process according to claim 3, wherein the reactor sequence comprises a prepolymerization reactor, at least one bulk reactor and at least one gas phase reactor, connected in series, in that order.

5. The process according to any of claims 1 – 4, wherein the cocatalyst component is an organoaluminium compound, preferably trialkyl aluminium, dialkyl aluminium chloride, alkyl aluminium sesquichloride, or a mixture thereof.

6. The process according to any of the preceding claims, wherein 10 to 40 wt-%, preferably 20 to 30 wt-% of the total cocatalyst component feed is fed to the first reaction zone and 90 to 60 wt-%, preferably 80 to 70 wt-% of the total cocatalyst component feed is fed to the second reaction zone.
7. The process according to any of claims 1 – 6, wherein the catalyst component contains magnesium, titanium, halogen and an electron donor.

8. The process according to claim 7, wherein the titanium in the catalyst component is in the form of TiCl$_3$ or TiCl$_4$.

9. The process according to any of the preceding claims, wherein the total molar ratio of aluminium in the cocatalyst component to titanium in the catalyst component is 200 – 500, preferably 200 – 350 and in particular 250 – 300.

10. The process according to claim 9, wherein the molar ratio of aluminium in the cocatalyst component to titanium in the catalyst component in the first feed of the cocatalyst component is 10 – 150, preferably 30 – 100 and in particular 40 – 80.

11. The process according to any of the preceding claims, wherein the total molar ratio of aluminium in the cocatalyst component to donor is 5 – 100, preferably 10 – 50 and in particular 10 – 30.

12. The process according to claim 11, wherein the molar ratio of aluminium in the cocatalyst component to the external donor is in the first feed of the cocatalyst component 1 – 10, preferably 1 – 5 and in particular 2 – 3.

13. The process according to any of the preceding claims, wherein the external donor is selected from the group consisting of dicyclopentyl dimethoxysilane, diisopropyl dimethoxysilane, methylcyclohexyl dimethoxysilane, di-isobutyl dimethoxysilane, and di-t-butyl dimethoxysilane, dicyclopentyl dimethoxysilane being particularly preferred.

14. The process according to any of the preceding claims, wherein bimodal propylene homopolymer is produced exhibiting a xylene soluble fraction of less than 1.8 wt-%, preferably less than 1.6 wt-%.

15. The process according to any of the preceding claims, wherein a propylene random copolymer is prepared exhibiting a xylene soluble fraction of less than 8 wt-%, preferably 1.5 – 5 wt-%.
16. The process according to any of the preceding claims, wherein a propylene polymer is prepared exhibiting a MFR₂ of 0.01 – 2000 g/10 min, preferably in 0.1 – 1000 g/10 min and in particular 1 – 400 g/10 min.

17. The process according to any of the preceding claims, wherein the polymer produced by the process is used for preparing polymer articles by moulding such as injection moulding, compression moulding, thermoforming, blow moulding, or foaming or extrusion.

18. A bimodal propylene polymer composition comprising a low molecular weight fraction and a high molecular weight fraction, which polymer is produced by
   - polymerizing propylene, optionally together with hydrogen and/or comonomers in a reaction sequence including at least one bulk reaction zone and at least one gas phase reaction zone arranged in series, in the presence of a Ziegler-Natta type catalyst including a catalyst component, a cocatalyst component and an external donor,
   - feeding said catalyst component, said external donor and a part of said cocatalyst component to a first reaction zone, and
   - feeding the rest of said cocatalyst component to a second reaction zone.

19. The polymer composition according to claim 18, characterized in that the propylene homopolymer exhibits a xylene soluble fraction of less than 1.8 wt-%, preferably less than 1.6 wt-%.
A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08F 10/06
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)

IPC7: C08F

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search: October 2000
Date of mailing of the international search report: 15.11.2000

Authorized officer: MONIKA BOHLIN/Els
Telephone No.
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<td>EP 0889064 A2 (BASF AKTIENGESELLSCHAFT), 7 January 1999 (07.01.99), column 1, line 19 - line 46; column 2, line 27 - column 3, line 8; column 3, line 38 - line 44, abstract, claims</td>
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