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(54) **Title:** POLYPROPYLENE FOR FILM APPLICATIONS

(57) **Abstract:** Propylene copolymer having a comonomer content in the range of 2.5 to 11.5 mol.-% and a melt flow rate MFR₂ (230 °C) in the range of 1.0 to 16.0 g/10min, wherein said propylene copolymer is featured by good toughness.



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Polypropylene for film applications

The present invention relates to a new propylene copolymer as well as unoriented films made therefrom. Further the present invention relates to the manufacture of said new propylene copolymer.

Propylene copolymers are very well known and quite often used in the field of film making. In this technical area polymers are required which combine high transparency and high impact strength. Quite often also high flowability of the used polymer is desired to reduce the process costs. However it is demanding to fulfill all the required demands with one polymer since the improvement of one property is paid on the expense of another property.

EP 0 663 422 defines a heterophasic system which is mixed with linear low density polyethylene. Accordingly this composition requires a complex mixture to achieve the demands in the technical field of films.

EP 1 664 162 defines a blown film with improved optical properties due to the specific selection of the nucleating agent. The improvement of properties due to the production of a specific propylene copolymer is not addressed.

Accordingly the object of the present invention is to provide a polymer which enables the skilled person to produce an unoriented film with good optical and mechanical properties in an efficient manner.

The finding of the present invention is to produce a propylene copolymer with rather high melt flow rate for polymers in film technology and being monophasic, while having a moderate to low randomness.

Accordingly the present invention is directed to a propylene copolymer (R-PP) having

- (a) a comonomer content in the range of 2.5 to 11.5 mol.-%;
- (b) a melt flow rate MFR₂ (230 °C) measured according to ISO 1133 in the range of 1.0 to 16.0 g/10min; and
- (c) a relative content of isolated to block ethylene sequences (I(E)) in the range of 45.0 to 69.0 %, wherein the I(E) content is defined by equation (I)

$$I(E) = \frac{f_{PEP}}{(f_{EEE} + f_{PEE} + f_{PEP})} \times 100 \quad (I)$$

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wherein

I(E) is the relative content of isolated to block ethylene sequences [in %];

fPEP is the mol fraction of propylene/ethylene/propylene sequences (PEP) in the sample;

5 fPEE is the mol fraction of propylene/ethylene/ethylene sequences (PEE) and of ethylene/ethylene/propylene sequences (EEP) in the sample;

fEEE is the mol fraction of ethylene/ethylene/ethylene sequences (EEE) in the sample

10 wherein all sequence concentrations being based on a statistical triad analysis of ^{13}C -NMR data.

Preferably the propylene copolymer (R-PP) is monophasic. Alternatively or additionally the propylene copolymer (R-PP) has preferably no glass transition temperature below -20 °C.

15 Surprisingly the propylene copolymer (R-PP) according to the invention has high impact and good optical properties even though the melt flow rate MFR_2 (230 °C) is relatively high.

20 Therefore in one specific embodiment the present invention is directed to an unoriented film comprising the propylene copolymer (R-PP) of the present invention. More preferably the present invention is directed to a cast film or a blown film, like air cooled blown film, comprising the propylene copolymer (R-PP) of the present invention.

In the following the propylene copolymer (R-PP) is defined in more detail.

25 As mentioned above the propylene copolymer (R-PP) according to this invention is preferably monophasic. Accordingly it is preferred that the propylene copolymer (R-PP) does not contain elastomeric (co)polymers forming inclusions as a second phase for improving mechanical properties. A polymer containing elastomeric (co)polymers as
30 insertions of a second phase would by contrast be called heterophasic and is preferably not part of the present invention. The presence of second phases or the so called inclusions are for instance visible by high resolution microscopy, like electron microscopy or atomic force microscopy, or by dynamic mechanical thermal analysis (DMTA). Specifically in DMTA the

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presence of a multiphase structure can be identified by the presence of at least two distinct glass transition temperatures.

Accordingly it is preferred that the propylene copolymer (R-PP) according to this invention
5 has no glass transition temperature below -30, preferably below -25 °C, more preferably below -20 °C.

On the other hand, in one preferred embodiment the propylene copolymer (R-PP) according to this invention has a glass transition temperature in the range of -12 to +2 °C, more
10 preferably in the range of -10 to +2 °C.

The propylene copolymer (R-PP) according to this invention has a melt flow rate MFR₂ (230 °C) measured according to ISO 1133 in the range of 1.0 to 16.0 g/10min, more preferably in the range of 1.0 to 12.0 g/10min, still more preferably in the range of 5.0 to
15 11.0 g/10min. In case the propylene copolymer (R-PP) shall be used in the cast film process the melt flow rate MFR₂ (230 °C) is preferably in the range of 6.0 to 16.0 g/10min, more preferably in the range of 7.0 to 11.0 g/10min. In turn, in case the propylene copolymer (R-PP) shall be used in the blown film process, like in the air cooled blown film process, the melt flow rate MFR₂ (230 °C) is preferably in the range of 1.0 to 4.0 g/10min, more
20 preferably in the range of 1.5 to 3.5 g/10min.

The propylene copolymer (R-PP) comprises apart from propylene also comonomers. Preferably the propylene copolymer (R-PP) comprises apart from propylene ethylene and/or C₄ to C₁₂ α -olefins. Accordingly the term "propylene copolymer" according to this invention
25 is preferably understood as a polypropylene comprising, preferably consisting of, units derivable from

(a) propylene

and

(b) ethylene and/or C₄ to C₁₂ α -olefins.

30

Thus the propylene copolymer (R-PP) according to this invention preferably comprises monomers copolymerizable with propylene, for example comonomers such as ethylene

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and/or C₄ to C₁₂ α-olefins, in particular ethylene and/or C₄ to C₈ α-olefins, e.g. 1-butene and/or 1-hexene. Preferably the propylene copolymer (R-PP) according to this invention comprises, especially consists of, monomers copolymerizable with propylene from the group consisting of ethylene, 1-butene and 1-hexene. More specifically the propylene copolymer (R-PP) of this invention comprises - apart from propylene - units derivable from ethylene and/or 1-butene. In a preferred embodiment the propylene copolymer (R-PP) according to this invention comprises units derivable from ethylene and propylene only.

Additionally it is appreciated that the propylene copolymer (R-PP) preferably has a comonomer content in a very specific range which contributes to the impact strength and the good optical properties. Thus it is required that the comonomer content of the propylene copolymer (R-PP) is in the range of 2.5 to below 11.5 mol.-%, more preferably in the range of 3.5 to below 11.0 mol.-%, still more preferably in the range of 5.5 to 10.5 mol.-%, yet more preferably in the range of 6.5 to 10.0 mol.-%.

Further the propylene copolymer is featured by its relative content of isolated to block ethylene sequences (I(E)). The I(E) content [%] is defined by equation (I)

$$I(E) = \frac{f_{PEP}}{(f_{EEE} + f_{PEE} + f_{PEP})} \times 100 \quad (I)$$

wherein

I(E) is the relative content of isolated to block ethylene sequences [in %];
 f_{PEP} is the mol fraction of propylene/ethylene/propylene sequences (PEP) in the sample;
 f_{PEE} is the mol fraction of propylene/ethylene/ethylene sequences (PEE) and of ethylene/ethylene/propylene sequences (EEP) in the sample;
 f_{EEE} is the mol fraction of ethylene/ethylene/ethylene sequences (EEE) in the sample
 wherein all sequence concentrations being based on a statistical triad analysis of ¹³C-NMR data.

Accordingly it is preferred that the propylene copolymer (R-PP) has a I(E) content in the range 45.0 to 69.0 %, more preferably in the range of 50.0 to 68.0 %, still more preferably in the range of 52.0 to 67.0 %.

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Further the propylene copolymer (R-PP) has a melting temperature of at least 135 °C, more preferably in the range of 135 to 155 °C, still more preferably in the range of 138 to 150 °C, like in the range of 138 to 145 °C.

5 Further it is preferred that the propylene copolymer (R-PP) has a crystallization temperature of at least 99 °C, more preferably in the range of 99 to 110 °C, still more preferably in the range of 100 to 108 °C, like in the range of 101 to 106 °C. These values are especially applicable in case the propylene copolymer (R-PP) is not nucleated, e.g. α -nucleated.

10 Preferably, the propylene copolymer (R-PP) has a xylene cold soluble fraction (XCS) in the range of 4.0 to 25.0 wt.-%, preferably in the range of 8.0 to 22.0 wt.-%, more preferably in the range of 10.0 to 21.0 wt.-%.

Preferably the propylene copolymer (R-PP) has a molecular weight distribution (Mw/Mn) of
15 at least 2.0, more preferably in the range of 2.5 to 6.5, still more preferably in the range of 2.8 to 5.5.

Additionally or alternatively to the molecular weight distribution (Mw/Mn) as defined in the previous paragraph the propylene copolymer (R-PP) has preferably weight average
20 molecular weight Mw in the range of 120 to 700 kg/mol, more preferably in the range of 150 to 600 kg/mol, like in the range of 180 to 500 kg/mol.

Preferably the propylene copolymer according to this invention has been produced in the presence of a Ziegler-Natta catalyst. The catalyst influences in particular the microstructure
25 of the polymer. In particular, polypropylenes prepared by using a metallocene catalyst provide a different microstructure compared to polypropylenes prepared by using Ziegler-Natta (ZN) catalysts. The most significant difference is the presence of regio-defects in metallocene-made polypropylenes which is not the case for polypropylenes made by Ziegler-Natta (ZN). The regio-defects can be of three different types, namely 2,1-erythro
30 (2,1e), 2,1-threo (2,1t) and 3,1 defects. A detailed description of the structure and mechanism of formation of regio-defects in polypropylene can be found in Chemical Reviews 2000,100(4),pages 1316-1327.

The term “2,1 regio defects” as used in the present invention defines the sum of 2,1 erythro regio-defects and 2,1 threo regio-defects.

- 5 Accordingly it is preferred that the propylene copolymer (R-PP) according to this invention has 2,1 regio-defects, like 2,1 erythro regio-defects, of at most 0.4 %, more preferably of at most 0.3 %, still more preferably of at most 0.2 %, determined by ¹³C-NMR spectroscopy. In one specific embodiment no 2,1 regio-defects, like 2,1 erythro regio-defects, are detectable for the propylene copolymer (R-PP).

10

The propylene copolymer (R-PP) preferably comprises at least two polymer fractions, like two or three polymer fraction, all of them being propylene copolymers. Preferably the random propylene copolymer (R-PP) comprises at least two different propylene copolymer fractions, like two different propylene copolymer fractions, wherein further the two

- 15 propylene copolymer fractions preferably differ in the comonomer content.

Preferably one fraction of the two polymer copolymer fractions of the propylene copolymer (R-PP) is the commoner lean fraction and the other fraction is the comonomer rich fraction, wherein more preferably the lean fraction and the rich fraction fulfill together in-equation

- 20 (II), more preferably in-equation (IIa), still more preferably in-equation (IIb),

$$\frac{Co (rich)}{Co (lean)} \geq 1.0 \text{ (II),}$$

$$1.0 \leq \frac{Co (rich)}{Co (lean)} \leq 5.0 \text{ (IIa),}$$

$$1.5 \leq \frac{Co (rich)}{Co (lean)} \leq 4.0 \text{ (IIb)}$$

wherein

- 25 Co (lean) is the comonomer content [mol.-%] of the propylene copolymer fraction with the lower comonomer content,
Co (rich) is the comonomer content [mol.-%] of the propylene copolymer fraction with the higher comonomer content.

- 30 Thus in one embodiment the first random propylene copolymer fraction (R-PP1) has higher comonomer content than the second random propylene copolymer fraction (R-PP2).

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In another embodiment the first random propylene copolymer fraction (R-PP1) has lower comonomer content than the second random propylene copolymer fraction (R-PP2). This embodiment is preferred.

5

Accordingly it is preferred that the first random propylene copolymer fraction (R-PP1) and the second random propylene copolymer fraction (R-PP2) fulfill together the in-equation (III), more preferably in-equation (IIIa), still more preferably in-equation (IIIb),

$$\frac{Co(R-PP2)}{Co(R-PP1)} \geq 1.0 \quad (III),$$

$$1.0 \leq \frac{Co(R-PP2)}{Co(R-PP1)} \leq 5.0 \quad (IIIa),$$

$$1.5 \leq \frac{Co(R-PP2)}{Co(R-PP1)} \leq 4.0 \quad (IIIb)$$

wherein

Co (R-PP1) is the comonomer content [mol.-%] of the first propylene copolymer fraction (R-PP1),

15 Co (R-PP2) is the comonomer content [mol.-%] of the second propylene copolymer fraction (R-PP2).

It is especially preferred that the propylene copolymer (R-PP) has higher comonomer content than the first random propylene copolymer fraction (R-PP1). Accordingly the random
20 propylene copolymer (R-PP) comprises, preferably consists of, the first random propylene copolymer fraction (R-PP1) and the second random propylene copolymer fraction (R-PP2), wherein further the random propylene copolymer (R-PP) fulfills the in-equation (IV), more preferably in-equation (IVa), still more preferably in-equation (IVb),

$$\frac{Co(R-PP)}{Co(R-PP1)} \geq 1.0 \quad (IV),$$

$$1.0 \leq \frac{Co(R-PP)}{Co(R-PP1)} \leq 4.0 \quad (IVa),$$

$$1.0 \leq \frac{Co(R-PP)}{Co(R-PP1)} \leq 3.0 \quad (IVb)$$

wherein

Co (R-PP1) is the comonomer content [mol.-%] of the first random propylene copolymer fraction (R-PP1),

30 Co (R-PP) is the comonomer content [mol.-%] of the propylene copolymer (R-PP).

Thus it is preferred that the first random propylene copolymer fraction (R-PP1) has a comonomer content of equal or below 7.0 mol-%, more preferably in the range 1.0 to 6.5 mol-%, yet more preferably in the range 2.0 to 6.2 mol-%, still more preferably in the range 3.5 to 6.0 mol-%.

On the other hand the second random propylene copolymer fraction (R-PP2) preferably has a comonomer content in the range of more than 7.0 to 15.0 mol-%, still more preferably in the range 8.0 to 14.0 mol-%, yet more preferably in the range 9.0 to 13.0 mol-%.

Preferably the first random propylene copolymer fraction (R-PP1) and the second random propylene copolymer fraction (R-PP2) have essentially the same melt flow rate MFR_2 (230 °C). Accordingly reference is made to the melt flow rate provided for the propylene copolymer (R-PP).

The comonomers of the first propylene copolymer fraction (R-PP1) and random propylene copolymer fraction (R-PP2), respectively, copolymerizable with propylene are ethylene and/or C_4 to C_{12} α -olefins, in particular ethylene and/or C_4 to C_8 α -olefins, e.g. 1-butene and/or 1-hexene. Preferably the first propylene copolymer fraction (R-PP1) and second propylene copolymer fraction (R-PP2), respectively, comprise, especially consist of, monomers copolymerizable with propylene from the group consisting of ethylene, 1-butene and 1-hexene. More specifically the first propylene copolymer fraction (R-PP1) and second propylene copolymer fraction (R-PP2), respectively, comprise - apart from propylene - units derivable from ethylene and/or 1-butene. In a preferred embodiment the first propylene copolymer fraction (R-PP1) and the second propylene copolymer fraction (R-PP2) comprise the same comonomers, i.e. ethylene only.

Preferably the weight ratio between the first propylene copolymer fraction (R-PP1) and the second propylene copolymer fraction (R-PP2) is 20/80 to 80/20, more preferably 30/70 to 70/30, like 35/65 to 65/35.

The propylene copolymer (R-PP) as defined in the instant invention may contain up to 5.0 wt.-% additives, like α -nucleating agents and antioxidants, as well as slip agents and antiblocking agents. Preferably the additive content (without α -nucleating agents) is below 3.0 wt.-%, like below 1.0 wt.-%.

5

Preferably the propylene copolymer (R-PP) comprises a α -nucleating agent. Even more preferred the present invention is free of β -nucleating agents. The α -nucleating agent is preferably selected from the group consisting of

- (i) salts of monocarboxylic acids and polycarboxylic acids, e.g. sodium benzoate or
10 aluminum tert-butylbenzoate, and
- (ii) dibenzylidenesorbitol (e.g. 1,3 : 2,4 dibenzylidenesorbitol) and C₁-C₈-alkyl-
substituted dibenzylidenesorbitol derivatives, such as methylidibenzylidenesorbitol,
ethylidibenzylidenesorbitol or dimethylidibenzylidenesorbitol (e.g. 1,3 : 2,4
15 di(methylbenzylidene) sorbitol), or substituted nonitol-derivatives, such as 1,2,3,-
trideoxy-4,6:5,7-bis-O-[(4-propylphenyl)methylene]-nonitol, and
- (iii) salts of diesters of phosphoric acid, e.g. sodium 2,2'-methylenebis (4, 6,-di-tert-
butylphenyl) phosphate or aluminium-hydroxy-bis[2,2'-methylene-bis(4,6-di-t-
butylphenyl)phosphate], and
- (iv) vinylcycloalkane polymer and vinylalkane polymer, and
- 20 (v) mixtures thereof.

Such additives are generally commercially available and are described, for example, in "Plastic Additives Handbook", 5th edition, 2001 of Hans Zweifel.

- 25 Preferably the propylene copolymer (R-PP) contains up to 2.0 wt.-% of the α -nucleating agent. In a preferred embodiment, the the propylene copolymer (R-PP) contains not more than 3000 ppm, more preferably of 1 to 3000 ppm, more preferably of 5 to 2000 ppm of a α -nucleating agent, in particular selected from the group consisting of dibenzylidenesorbitol (e.g. 1,3 : 2,4 dibenzylidene sorbitol), dibenzylidenesorbitol derivative, preferably
- 30 dimethylidibenzylidenesorbitol (e.g. 1,3 : 2,4 di(methylbenzylidene) sorbitol), or substituted nonitol-derivatives, such as 1,2,3,-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl)methylene]-nonitol, vinylcycloalkane polymer, vinylalkane polymer, and mixtures thereof.

The present invention is not only directed to the instant propylene copolymer (R-PP) but also to unoriented films made therefrom. Accordingly in a further embodiment the present invention is directed to unoriented films, like cast films or blown films, e.g. air cooled blown
5 films, comprising at least 70 wt.-%, preferably comprising at least 80 wt.-%, more preferably comprising at least 90 wt.-%, still more preferably comprising at least 95 wt.-%, yet more preferably comprising at least 99 wt.-%, of the instant propylene copolymer (R-PP).

One distinguishes between unoriented and oriented films (see for instance polypropylene
10 handbook, Nello Pasquini, 2nd edition, Hanser). Oriented films are typically biaxially oriented films, whereas unoriented films are cast or blown films, e.g. air cooled blown films. Accordingly an unoriented film is not drawn intensively in machine and transverse direction as done by oriented films. Thus the unoriented film according to this invention is not a biaxially oriented film. Preferably the unoriented film according to the instant invention is a
15 cast film or blown film, the latter being preferred. In one specific embodiment the unoriented film is an air-cooled blown film.

Preferably the unoriented film has a thickness of 5 to 2,000 μm , preferably of 10 to 1,000 μm , more preferably of 20 to 700 μm , like of 40 to 500 μm .
20

The present invention is also directed to the use of the propylene copolymer (R-PP) in the manufacture of unoriented films, like cast films or blown films, e.g. air cooled blown films.

In case unoriented film is produced by cast film technology the molten propylene copolymer
25 (R-PP) is extruded through a slot extrusion die onto a chill roll to cool the polymer to a solid film. Typically the propylene copolymer (R-PP) is firstly compressed and liquefied in an extruder, it being possible for any additives to be already added to the polymer or introduced at this stage via a masterbatch. The melt is then forced through a flat-film die (slot die), and the extruded film is taken off on one or more take-off rolls, during which it cools and
30 solidifies. It has proven particularly favorable to keep the take-off roll or rolls, by means of which the extruded film is cooled and solidified, at a temperature from 10 to 50°C, preferably from 15 to 40°C.

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In the blown film process the propylene copolymer (R-PP) melt is extruded through an annular die and blown into a tubular film by forming a bubble which is collapsed between nip rollers after solidification. The blown extrusion can be preferably effected at a
5 temperature in the range 160 to 240 °C, and cooled by water or preferably by blowing gas (generally air) at a temperature of 10 to 50 °C to provide a frost line height of 0.5 to 8 times the diameter of the die. The blow up ratio should generally be in the range of from 1.5 to 4, such as from 2 to 4, preferably 2.5 to 3.5.

10 The propylene copolymer (R-PP) according to this invention is preferably produced in a sequential polymerization process in the presence of a Ziegler-Natta catalyst as defined below.

Accordingly it is preferred that the propylene copolymer (R-PP) is produced in the presence
15 of

- (a) a Ziegler-Natta catalyst (ZN-C) comprises a titanium compound (TC), a magnesium compound (MC) and an internal donor (ID), wherein said internal donor (ID) is a non-phthalic acid ester,
- (b) optionally a co-catalyst (Co), and
- 20 (c) optionally an external donor (ED).

Preferably the propylene copolymer (R-PP) is produced in a sequential polymerization process comprising at least two reactors (R1) and (R2), in the first reactor (R1) the first propylene copolymer fraction (R-PP1) is produced and subsequently transferred into the
25 second reactor (R2), in the second reactor (R2) the second propylene copolymer fraction (R-PP2) is produced in the presence of the first propylene copolymer fraction (R-PP1).

The term “sequential polymerization system” indicates that the propylene copolymer (R-PP) is produced in at least two reactors connected in series. Accordingly the present
30 polymerization system comprises at least a first polymerization reactor (R1) and a second polymerization reactor (R2), and optionally a third polymerization reactor (R3). The term “polymerization reactor” shall indicate that the main polymerization takes place. Thus in

case the process consists of two polymerization reactors, this definition does not exclude the option that the overall system comprises for instance a pre-polymerization step in a pre-polymerization reactor. The term "consist of" is only a closing formulation in view of the main polymerization reactors.

5

Preferably at least one of the two polymerization reactors (R1) and (R2) is a gas phase reactor (GPR). Still more preferably the second polymerization reactor (R2) and the optional third polymerization reactor (R3) are gas phase reactors (GPRs), i.e. a first gas phase reactor (GPR1) and a second gas phase reactor (GPR2). A gas phase reactor (GPR) according to this
10 invention is preferably a fluidized bed reactor, a fast fluidized bed reactor or a settled bed reactor or any combination thereof.

Accordingly, the first polymerization reactor (R1) is preferably a slurry reactor (SR) and can be any continuous or simple stirred batch tank reactor or loop reactor operating in bulk or
15 slurry. Bulk means a polymerization in a reaction medium that comprises of at least 60 % (w/w) monomer. According to the present invention the slurry reactor (SR) is preferably a (bulk) loop reactor (LR). Accordingly the average concentration of propylene copolymer (R-PP), i.e. the first fraction (1st F) of the propylene copolymer (R-PP) (i.e. the first propylene copolymer fraction (R-PP1)), in the polymer slurry within the loop reactor (LR) is typically
20 from 15 wt.-% to 55 wt.-%, based on the total weight of the polymer slurry within the loop reactor (LR). In one preferred embodiment of the present invention the average concentration of the first propylene copolymer fraction (R-PP1) in the polymer slurry within the loop reactor (LR) is from 20 wt.-% to 55 wt.-% and more preferably from 25 wt.-% to 52 wt.-%, based on the total weight of the polymer slurry within the loop reactor (LR).

25

Preferably the propylene copolymer of the first polymerization reactor (R1), i.e. the first propylene copolymer fraction (R-PP1), more preferably the polymer slurry of the loop reactor (LR) containing the first propylene copolymer fraction (R-PP1), is directly fed into the second polymerization reactor (R2), i.e. into the (first) gas phase reactor (GPR1), without
30 a flash step between the stages. This kind of direct feed is described in EP 887379 A, EP 887380 A, EP 887381 A and EP 991684 A. By "direct feed" is meant a process wherein the content of the first polymerization reactor (R1), i.e. of the loop reactor (LR), the polymer

slurry comprising the the first propylene copolymer fraction (R-PP1), is led directly to the next stage gas phase reactor.

Alternatively, the propylene copolymer of the first polymerization reactor (R1), i.e. the first
5 propylene copolymer fraction (R-PP1), more preferably polymer slurry of the loop reactor (LR) containing the first propylene copolymer fraction (R-PP1), may be also directed into a flash step or through a further concentration step before fed into the second polymerization reactor (R2), i.e. into the gas phase reactor (GPR). Accordingly, this "indirect feed" refers to a process wherein the content of the first polymerization reactor (R1), of the loop reactor
10 (LR), i.e. the polymer slurry, is fed into the second polymerization reactor (R2), into the (first) gas phase reactor (GPR1), via a reaction medium separation unit and the reaction medium as a gas from the separation unit.

More specifically, the second polymerization reactor (R2), and any subsequent reactor, for
15 instance the third polymerization reactor (R3), are preferably gas phase reactors (GPRs). Such gas phase reactors (GPR) can be any mechanically mixed or fluid bed reactors. Preferably the gas phase reactors (GPRs) comprise a mechanically agitated fluid bed reactor with gas velocities of at least 0.2 m/sec. Thus it is appreciated that the gas phase reactor is a fluidized bed type reactor preferably with a mechanical stirrer.

20 Thus in a preferred embodiment the first polymerization reactor (R1) is a slurry reactor (SR), like loop reactor (LR), whereas the second polymerization reactor (R2) and any optional subsequent reactor, like the third polymerization reactor (R3), are gas phase reactors (GPRs). Accordingly for the instant process at least two, preferably two polymerization reactors (R1) and (R2) or three polymerization reactors (R1), (R2) and (R3), namely a slurry reactor (SR),
25 like loop reactor (LR) and a (first) gas phase reactor (GPR1) and optionally a second gas phase reactor (GPR2), connected in series are used. If needed prior to the slurry reactor (SR) a pre-polymerization reactor is placed.

30 The Ziegler-Natta catalyst (ZN-C) is fed into the first polymerization reactor (R1) and is transferred with the polymer (slurry) obtained in the first polymerization reactor (R1) into the subsequent reactors. If the process covers also a pre-polymerization step it is preferred

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that all of the Ziegler-Natta catalyst (ZN-C) is fed in the pre-polymerization reactor.

Subsequently the pre-polymerization product containing the Ziegler-Natta catalyst (ZN-C) is transferred into the first polymerization reactor (R1).

- 5 A preferred multistage process is a “loop-gas phase”-process, such as developed by Borealis A/S, Denmark (known as BORSTAR® technology) described e.g. in patent literature, such as in EP 0 887 379, WO 92/12182 WO 2004/000899, WO 2004/111095, WO 99/24478, WO 99/24479 or in WO 00/68315.

- 10 A further suitable slurry-gas phase process is the Spheripol® process of Basell.

Especially good results are achieved in case the temperature in the reactors is carefully chosen.

- 15 Accordingly it is preferred that the operating temperature in the first polymerization reactor (R1) is in the range of 62 to 85 °C, more preferably in the range of 65 to 82 °C, still more preferably in the range of 67 to 80 °C.

- Alternatively or additionally to the previous paragraph it is preferred that the operating
20 temperature in the second polymerization reactor (R2) and optional in the third reactor (R3) is in the range of 75 to 95 °C, more preferably in the range of 78 to 92 °C.

- Preferably the operating temperature in the second polymerization reactor (R2) is equal or higher to the operating temperature in the first polymerization reactor (R1). Accordingly it is
25 preferred that the operating temperature

- (a) in the first polymerization reactor (R1) is in the range of 62 to 85 °C, more preferably in the range of 65 to 82 °C, still more preferably in the range of 67 to 80 °C, and
(b) in the second polymerization reactor (R2) is in the range of 75 to 95 °C, more
30 preferably in the range of 78 to 92 °C, still more preferably in the range of 78 to 88 °C, with the proviso that the operating temperature in the in the second polymerization reactor (R2) is equal or higher to the operating temperature in the first polymerization reactor (R1).

Still more preferably the operating temperature of the third polymerization reactor (R3) – if present – is higher than the operating temperature in the first polymerization reactor (R1). In one specific embodiment the operating temperature of the third polymerization reactor (R3) – if present – is higher than the operating temperature in the first polymerization reactor (R1) and in the second polymerization reactor (R2). Accordingly it is preferred that the operating temperature

(a) in the first polymerization reactor (R1) is in the range of 62 to 85 °C, more preferably in the range of 65 to 82 °C, still more preferably in the range of 67 to 80 °C,

(b) in the second polymerization reactor (R2) is in the range of 75 to 95 °C, more preferably in the range of 78 to 92 °C, still more preferably in the range of 78 to 88 °C, and

(c) in the third polymerization reactor (R3) – if present - is in the range of 75 to 95 °C, more preferably in the range of 78 to 92 °C, still more preferably in the range of 85 to 92 °C, like in the range of 87 to 92 °C,

with the proviso that the operating temperature in the in the second polymerization reactor (R2) is equal or higher to the operating temperature in the first polymerization reactor (R1) and

with the proviso that the third polymerization reactor (R3) is higher than the operating temperature in the first polymerization reactor (R1), preferably is higher than the operating temperature in the first polymerization reactor (R1) and in the second polymerization reactor (R2).

Typically the pressure in the first polymerization reactor (R1), preferably in the loop reactor (LR), is in the range of from 20 to 80 bar, preferably 30 to 70 bar, like 35 to 65 bar, whereas the pressure in the second polymerization reactor (R2), i.e. in the (first) gas phase reactor (GPR1), and optionally in any subsequent reactor, like in the third polymerization reactor (R3), e.g. in the second gas phase reactor (GPR2), is in the range of from 5 to 50 bar, preferably 15 to 40 bar.

30

Preferably hydrogen is added in each polymerization reactor in order to control the molecular weight, i.e. the melt flow rate MFR₂.

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Preferably the average residence time is rather long in the polymerization reactors (R1) and (R2). In general, the average residence time (τ) is defined as the ratio of the reaction volume (V_R) to the volumetric outflow rate from the reactor (Q_o) (i.e. V_R/Q_o), i.e. $\tau = V_R/Q_o$ [tau =
5 V_R/Q_o]. In case of a loop reactor the reaction volume (V_R) equals to the reactor volume.

Accordingly the average residence time (τ) in the first polymerization reactor (R1) is preferably at least 20 min, more preferably in the range of 20 to 45 min, still more preferably in the range of 25 to 42 min, like in the range of 28 to 40 min, and/or the average residence
10 time (τ) in the second polymerization reactor (R2) is preferably at least 90 min, more preferably in the range of 90 to 220 min, still more preferably in the range of 100 to 210 min, yet more preferably in the range of 105 to 200 min, like in the range of 105 to 190 min.
Preferably the average residence time (τ) in the third polymerization reactor (R3) – if present – is preferably at least 30 min, more preferably in the range of 30 to 90 min, still more
15 preferably in the range of 40 to 80 min, like in the range of 50 to 80 min.

Further it is preferred that the average residence time (τ) in the total sequential polymerization system, more preferably that the average residence time (τ) in the first (R1) second polymerization reactors (R2) and optional third polymerization reactor (R3) together,
20 is at least 140 min, more preferably at least 150 min, still more preferably in the range of 140 to 240 min, more preferably in the range of 150 to 220 min, still more preferably in the range of 155 to 220 min.

As mentioned above the instant process can comprises in addition to the (main)
25 polymerization of the propylene copolymer (R-PP) in the at least two polymerization reactors (R1, R3 and optional R3) prior thereto a pre-polymerization in a pre-polymerization reactor (PR) upstream to the first polymerization reactor (R1).

In the pre-polymerization reactor (PR) a polypropylene (Pre-PP) is produced. The pre-
30 polymerization is conducted in the presence of the Ziegler-Natta catalyst (ZN-C). According to this embodiment the Ziegler-Natta catalyst (ZN-C), the co-catalyst (Co), and the external donor (ED) are all introduced to the pre-polymerization step. However, this shall not exclude

the option that at a later stage for instance further co-catalyst (Co) and/or external donor (ED) is added in the polymerization process, for instance in the first reactor (R1). In one embodiment the Ziegler-Natta catalyst (ZN-C), the co-catalyst (Co), and the external donor (ED) are only added in the pre-polymerization reactor (PR), if a pre-polymerization is
5 applied.

The pre-polymerization reaction is typically conducted at a temperature of 0 to 60 °C, preferably from 15 to 50 °C, and more preferably from 20 to 45 °C.

10 The pressure in the pre-polymerization reactor is not critical but must be sufficiently high to maintain the reaction mixture in liquid phase. Thus, the pressure may be from 20 to 100 bar, for example 30 to 70 bar.

In a preferred embodiment, the pre-polymerization is conducted as bulk slurry
15 polymerization in liquid propylene, i.e. the liquid phase mainly comprises propylene, with optionally inert components dissolved therein. Furthermore, according to the present invention, an ethylene feed is employed during pre-polymerization as mentioned above.

It is possible to add other components also to the pre-polymerization stage. Thus, hydrogen
20 may be added into the pre-polymerization stage to control the molecular weight of the polypropylene (Pre-PP) as is known in the art. Further, antistatic additive may be used to prevent the particles from adhering to each other or to the walls of the reactor.

The precise control of the pre-polymerization conditions and reaction parameters is within
25 the skill of the art.

Due to the above defined process conditions in the pre-polymerization, preferably a mixture (MI) of the Ziegler-Natta catalyst (ZN-C) and the polypropylene (Pre-PP) produced in the pre-polymerization reactor (PR) is obtained. Preferably the Ziegler-Natta catalyst (ZN-C) is
30 (finely) dispersed in the polypropylene (Pre-PP). In other words, the Ziegler-Natta catalyst (ZN-C) particles introduced in the pre-polymerization reactor (PR) split into smaller fragments which are evenly distributed within the growing polypropylene (Pre-PP). The

sizes of the introduced Ziegler-Natta catalyst (ZN-C) particles as well as of the obtained fragments are not of essential relevance for the instant invention and within the skilled knowledge.

- 5 As mentioned above, if a pre-polymerization is used, subsequent to said pre-polymerization, the mixture (MI) of the Ziegler-Natta catalyst (ZN-C) and the polypropylene (Pre-PP) produced in the pre-polymerization reactor (PR) is transferred to the first reactor (R1). Typically the total amount of the polypropylene (Pre-PP) in the final propylene copolymer (R-PP) is rather low and typically not more than 5.0 wt.-%, more preferably not more than
- 10 4.0 wt.-%, still more preferably in the range of 0.5 to 4.0 wt.-%, like in the range 1.0 of to 3.0 wt.-%.

- In case that pre-polymerization is not used propylene and the other ingredients such as the Ziegler-Natta catalyst (ZN-C) are directly introduced into the first polymerization reactor
- 15 (R1).

Accordingly the process according the instant invention comprises the following steps under the conditions set out above

- (a) in the first polymerization reactor (R1), i.e. in a loop reactor (LR), propylene and a
- 20 comonomer being ethylene and/or a C₄ to C₁₂ α -olefin, preferably propylene and ethylene, are polymerized obtaining a first propylene copolymer fraction (R-PP1) of the propylene copolymer (R-PP),
- (b) transferring said first propylene copolymer fraction (R-PP1) to a second polymerization reactor (R2),
- 25 (c) in the second polymerization reactor (R2) propylene and a comonomer being ethylene and/or a C₄ to C₁₂ α -olefin, preferably propylene and ethylene, are polymerized in the presence of the first propylene copolymer fraction (R-PP1) obtaining a second propylene copolymer fraction (R-PP2) of the propylene copolymer (R-PP), said first propylene copolymer fraction (R-PP1) and said second propylene copolymer fraction (R-PP2) form the
- 30 propylene copolymer (R-PP).

A pre-polymerization as described above can be accomplished prior to step (a).

The Ziegler-Natta Catalyst (ZN-C), the external donor (ED) and the co-catalyst (Co)

As pointed out above in the specific process for the preparation of the propylene copolymer (R-PP) as defined above a Ziegler-Natta catalyst (ZN-C) must be used. Accordingly the Ziegler-Natta catalyst (ZN-C) will be now described in more detail.

The catalyst used in the present invention is a solid Ziegler-Natta catalyst (ZN-C), which comprises a titanium compound (TC), a magnesium compound (MC) and an internal donor (ID), wherein said internal donor (ID) is a non-phthalic acid ester, most preferably diester of non-phthalic dicarboxylic acids as described in more detail below. Thus, the catalyst used in the present invention is fully free of undesired phthalic compounds.

The Ziegler-Natta catalyst (ZN-C) can be further defined by the way as obtained. Accordingly the Ziegler-Natta catalyst (ZN-C) is preferably obtained by a process comprising the steps of

- a) providing a solution of at least one complex (A) being a complex of a magnesium compound (MC) and an alcohol comprising in addition to the hydroxyl moiety at least one further oxygen bearing moiety (A1) being different to a hydroxyl group, and optionally at least one complex (B) being a complex of said magnesium compound (MC) and an alcohol not comprising any other oxygen bearing moiety (B1),
- b) combining said solution with a titanium compound (TC) and producing an emulsion the dispersed phase of which contains more than 50 mol.-% of the magnesium;
- c) agitating the emulsion in order to maintain the droplets of said dispersed phase preferably within an average size range of 5 to 200µm;
- d) solidifying said droplets of the dispersed phase;
- e) recovering the solidified particles of the olefin polymerisation catalyst component, and wherein an internal donor (ID) is added at any step prior to step c) and said internal donor (ID) is non-phthalic acid ester, preferably said internal donor (ID) is a diester of non-phthalic dicarboxylic acids as described in more detail below.

Detailed description as to how such a Ziegler-Natta catalyst (ZN-C) can be obtained is disclosed in WO 2012/007430.

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In a preferred embodiment in step a) the solution of complex of magnesium compound (MC) is a mixture of complexes of magnesium compound (MC) (complexes (A) and (B)).

- 5 The complexes of magnesium compound (MC) (complexes (A) and (B)) can be prepared *in situ* in the first step of the catalyst preparation process by reacting said magnesium compound (MC) with the alcohol(s) as described above and in more detail below, or said complexes can be separately prepared complexes, or they can be even commercially available as ready complexes and used as such in the catalyst preparation process of the
- 10 invention. In case the mixture of complexes of magnesium compound (MC) (complexes (A) and (B)) are prepared *in situ* in the first step of the catalyst preparation process they are preferably prepared by reacting said magnesium compound (MC) with the mixture of alcohols (A1) and (B1).
- 15 Preferably, the alcohol (A1) comprising in addition to the hydroxyl moiety at least one further oxygen bearing group different to a hydroxyl group to be employed in accordance with the present invention is an alcohol bearing an ether group.

- Illustrative examples of such preferred alcohols (A1) comprising in addition to the hydroxyl
- 20 moiety at least one further oxygen bearing group to be employed in accordance with the present invention are glycol monoethers, in particular C₂ to C₄ glycol monoethers, such as ethylene or propylene glycol monoethers wherein the ether moieties comprise from 2 to 18 carbon atoms, preferably from 4 to 12 carbon atoms. Preferred monoethers are C₂ to C₄ glycol monoethers and derivatives thereof. Illustrative and preferred examples are 2-(2-
- 25 ethylhexyloxy)ethanol, 2-butyloxy ethanol, 2-hexyloxy ethanol and 1,3-propylene-glycol-monobutyl ether, 3-butoxy-2-propanol, with 2-(2-ethylhexyloxy)ethanol and 1,3-propylene-glycol-monobutyl ether, 3-butoxy-2-propanol being particularly preferred.

- In case a mixture of complexes (A) and (B) (or alcohols (A1) and (B1) respectively) are
- 30 used, the different complexes or alcohols are usually employed in a mole ratio of A:B, or A1:B1 from 1.0:10 to 1.0:0.5, preferably this mole ratio is from 1.0:8.0 to 1.0:1.0, more preferably 1.0:6.0 to 1.0:2.0, even more preferably 1.0:5.0 to 1.0:3.0. As indicated in the

ratios above it is more preferred that the amount of alcohol A1, preferably alcohol with ether moiety, is higher than alcohol B1, i.e. alcohol without any other oxygen bearing moiety different to hydroxyl.

5 The internal donor (ID) used in the preparation of the Ziegler-Natta catalyst (ZN-C) is preferably selected from (di)esters of non-phthalic carboxylic (di)acids and derivatives and mixtures thereof. The ester moieties, i.e. the moieties derived from an alcohol (i.e. the alkoxy group of the ester), may be identical or different, preferably these ester moieties are identical. Typically the ester moieties are aliphatic or aromatic hydrocarbon groups. Preferred
10 examples thereof are linear or branched aliphatic groups having from 1 to 20 carbon atoms, preferably 2 to 16 carbon atoms, more preferably from 2 to 12 carbon atoms, or aromatic groups having 6 to 12 carbon atoms, optionally containing heteroatoms of Groups 14 to 17 of the Periodic Table of IUPAC, especially N, O, S and/or P. The acid moiety of the di- or monoacid(di)ester, preferably of the diester of diacid, preferably comprises 1 to 30 carbon
15 atoms, more preferably, 2 to 20 carbon atoms, still more preferably 2 to 16 carbon atoms, optionally being substituted by aromatic or saturated or non-saturated cyclic or aliphatic hydrocarbyls having 1 to 20 C, preferably 1 to 10 carbon atoms and optionally containing heteroatoms of Groups 14 to 17 of the Periodic Table of IUPAC, especially N, O, S and/or P. Especially preferred esters are diesters of mono-unsaturated dicarboxylic acids.

20 In particular preferred esters are esters belonging to a group comprising malonates, maleates, succinates, glutarates, cyclohexene-1,2-dicarboxylates and benzoates, optionally being substituted as defined below, and any derivatives and/or mixtures thereof. Preferred examples are e.g. substituted maleates and citraconates, most preferably citraconates.

25 The internal donor (ID) or precursor thereof as defined further below is added preferably in step a) to said solution.

Esters used as internal donors (ID) can be prepared as is well known in the art. As example
30 dicarboxylic acid diesters can be formed by simply reacting of a carboxylic diacid anhydride with a C₁-C₂₀ alkanol and/or diol.

The titanium compound (TC) is preferably a titanium halide, like TiCl_4 .

The complexes of magnesium compounds can be alkoxy magnesium complexes, preferably selected from the group consisting of magnesium dialkoxides, and complexes of a
5 magnesium dihalide and a magnesium dialkoxide. It may be a reaction product of an alcohol and a magnesium compound selected from the group consisting of dialkyl magnesiums, alkyl magnesium alkoxides and alkyl magnesium halides, preferably dialkyl magnesium. It can further be selected from the group consisting of dialkyloxy magnesiums, diaryloxy
10 magnesiums, alkyloxy magnesium halides, aryloxy magnesium halides, alkyl magnesium alkoxides, aryl magnesium alkoxides and alkyl magnesium aryloxides.

The magnesium dialkoxide may be the reaction product of a dialkyl magnesium of the formula R_2Mg , wherein each one of the two Rs is a similar or different $\text{C}_1\text{-C}_{20}$ alkyl, preferably a similar or different $\text{C}_2\text{-C}_{10}$ alkyl with alcohols as defined in the present
15 application. Typical magnesium alkyls are ethylbutyl magnesium, dibutyl magnesium, dipropyl magnesium, propylbutyl magnesium, dipentyl magnesium, butylpentyl magnesium, butyloctyl magnesium and dioctyl magnesium. Most preferably, one R of the formula R_2Mg is a butyl group and the other R is an octyl or ethyl group, i.e. the dialkyl magnesium compound is butyl octyl magnesium or butyl ethyl magnesium.

20 Typical alkyl-alkoxy magnesium compounds RMgOR , when used, are ethyl magnesium butoxide, butyl magnesium pentoxide, octyl magnesium butoxide and octyl magnesium octoxide.

25 Dialkyl magnesium or alkyl magnesium alkoxide can react, in addition to the alcohol containing in addition to the hydroxyl group at least one further oxygen bearing moiety being different to a hydroxyl moiety, which is defined above in this application, with a monohydric alcohol $\text{R}'\text{OH}$, or a mixture thereof with a polyhydric alcohol $\text{R}'(\text{OH})_m$

30 Preferred monohydric alcohols are alcohols of the formula $\text{R}^b(\text{OH})$, wherein R^b is a $\text{C}_1\text{-C}_{20}$, preferably a $\text{C}_4\text{-C}_{12}$, and most preferably a $\text{C}_6\text{-C}_{10}$, straight-chain or branched alkyl residue or a $\text{C}_6\text{-C}_{12}$ aryl residue. Preferred monohydric alcohols include methanol, ethanol, n-propanol,

iso-propanol, n-butanol, iso-butanol, sec-butanol, tert-butanol, n-amyl alcohol, iso-amyl alcohol, sec-amyl alcohol, tert-amyl alcohol, diethyl carbinol, sec-isoamyl alcohol, tert-butyl carbinol, 1-hexanol, 2-ethyl-1-butanol, 4-methyl-2-pentanol, 1-heptanol, 2-heptanol, 4-heptanol, 2,4-dimethyl-3-pentanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 5-nonanol, diisobutyl carbinol, 1-decanol and 2,7-dimethyl-2-octanol, 1-undecanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, 1-pentadecanol, 1-hexadecanol, 1-heptadecanol 1-octadecanol and phenol or benzyl alcohol. The aliphatic monohydric alcohols may optionally be unsaturated, as long as they do not act as catalyst poisons. The most preferred monohydric alcohol is 2-ethyl-1-hexanol.

10

Preferred polyhydric alcohols are alcohols of the formula $R^a(OH)_m$, wherein R^a is a straight-chain, cyclic or branched C_2 to C_6 hydrocarbon residue, (OH) denotes hydroxyl moieties of the hydrocarbon residue and m is an integer of 2 to 6, preferably 3 to 5. Especially preferred polyhydric alcohols include ethylene glycol, propylene glycol, trimethylene glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 2,3-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, pinacol, diethylene glycol, triethylene glycol, 1,2-catechol, 1,3-catechol and 1,4-catechol, and triols such as glycerol and pentaerythritol.

15

The solvents to be employed for the preparation of the Ziegler-Natta catalyst (ZN-C) may be selected among aromatic and aliphatic solvents or mixtures thereof. Preferably the solvents are aromatic and/or aliphatic hydrocarbons with 5 to 20 carbon atoms, preferably 5 to 16, more preferably 5 to 12 carbon atoms, examples of which include benzene, toluene, cumene, xylol and the like, with toluene being preferred, as well as pentane, hexane, heptane, octane and nonane including straight chain, branched and cyclic compounds, and the like, with hexanes and heptanes being particular preferred.

20

25

Mg compound (MC) is typically provided as a 10 to 50 wt-% solution in a solvent as indicated above. Typical commercially available MC solutions are 20 – 40 wt-% solutions in toluene or heptanes.

30

The reaction for the preparation of the complex of magnesium compound (MC) may be carried out at a temperature of 40° to 70°C.

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In step b) the solution of step a) is typically added to the titanium compound (TC), such as titanium tetrachloride. This addition preferably is carried out at a low temperature, such as from -10 to 40°C, preferably from -5 to 20°C, such as about -5°C to 15 °C.

5

The temperature for steps b) and c), is typically -10 to 50°C, preferably from -5 to 30°C, , while solidification typically requires heating as described in detail further below.

10 The emulsion, i.e. the two phase liquid-liquid system may be formed in all embodiments of the present invention by simple stirring and optionally adding (further) solvent(s) and additives, such as the turbulence minimizing agent (TMA) and/or the emulsifying agents described further below.

15 Preparation of the Ziegler-Natta catalyst (ZN-C) used in the present invention is based on a liquid/liquid two-phase system where no separate external carrier materials such as silica or MgCl_2 are needed in order to get solid catalyst particles.

20 The present Ziegler-Natta catalyst (ZN-C) particles are spherical and they have preferably a mean particle size from 5 to 500 μm , such as from 5 to 300 μm and in embodiments from 5 to 200 μm , or even from 10 to 100 μm . These ranges also apply for the droplets of the dispersed phase of the emulsion as described herein, taking into consideration that the droplet size can change (decrease) during the solidification step.

25 The process of the preparation of the Ziegler-Natta catalyst (ZN-C) as intermediate stage, yields to an emulsion of a denser, titanium compound (TC)/toluene-insoluble, oil dispersed phase typically having a titanium compound (TC)/magnesium mol ratio of 0.1 to 10 and an oil disperse phase having a titanium compound (TC)/magnesium mol ratio of 10 to 100. The titanium compound (TC) is preferably TiCl_4 . This emulsion is then typically agitated, optionally in the presence of an emulsion stabilizer and/or a turbulence minimizing agent, in
30 order to maintain the droplets of said dispersed phase, typically within an average size range of 5 to 200 μm . The catalyst particles are obtained after solidifying said particles of the dispersed phase e.g. by heating.

In effect, therefore, virtually the entirety of the reaction product of the Mg complex with the titanium compound (TC) - which is the precursor of the ultimate catalyst component - becomes the dispersed phase, and proceeds through the further processing steps to the final particulate form. The disperse phase, still containing a useful quantity of titanium compound (TC), can be reprocessed for recovery of that metal.

Furthermore, emulsifying agents/emulsion stabilizers can be used additionally in a manner known in the art for facilitating the formation and/or stability of the emulsion. For the said purposes e.g. surfactants, e.g. a class based on acrylic or methacrylic polymers can be used. Preferably, said emulsion stabilizers are acrylic or methacrylic polymers, in particular those with medium sized ester side chains having more than 10, preferably more than 12 carbon atoms and preferably less than 30, and preferably 12 to 20 carbon atoms in the ester side chain. Particular preferred are unbranched C₁₂ to C₂₀ (meth)acrylates such as poly(hexadecyl)-methacrylate and poly(octadecyl)-methacrylate.

Furthermore, in some embodiments a turbulence minimizing agent (TMA) can be added to the reaction mixture in order to improve the emulsion formation and maintain the emulsion structure. Said TMA agent has to be inert and soluble in the reaction mixture under the reaction conditions, which means that polymers without polar groups are preferred, like polymers having linear or branched aliphatic carbon backbone chains. Said TMA is in particular preferably selected from α -olefin polymers of α -olefin monomers with 6 to 20 carbon atoms, like polyoctene, polynonene, polydecene, polyundecene or polydodecene or mixtures thereof. Most preferable it is polydecene.

TMA can be added to the emulsion in an amount of e.g. 1 to 1.000 ppm, preferably 5 to 100 ppm and more preferable 5 to 50 ppm, based on the total weight of the reaction mixture.

It has been found that the best results are obtained when the titanium compound (TC)/Mg mol ratio of the dispersed phase (denser oil) is 1 to 5, preferably 2 to 4, and that of the disperse phase oil is 55 to 65. Generally the ratio of the mol ratio titanium compound (TC)/Mg in the disperse phase oil to that in the denser oil is at least 10.

Solidification of the dispersed phase droplets by heating is suitably carried out at a temperature of 70 to 150°C, usually at 80 to 110°C, preferably at 90 to 110°C. The heating may be done faster or slower. As especial slow heating is understood here heating with a heating rate of about 5°C/min or less, and especial fast heating e.g. 10°C/min or more. Often slower heating rates are preferable for obtaining good morphology of the catalyst component.

The solidified particulate product may be washed at least once, preferably at least twice, most preferably at least three times with a hydrocarbon, which preferably is selected from aromatic and aliphatic hydrocarbons, preferably with toluene, heptane or pentane. Washings can be done with hot (e.g. 90°C) or cold (room temperature) hydrocarbons or combinations thereof.

Finally, the washed Ziegler-Natta catalyst (ZN-C) is recovered. It can further be dried, as by evaporation or flushing with nitrogen, or it can be slurried to an oily liquid without any drying step.

The finally obtained Ziegler-Natta catalyst (ZN-C) is desirably in the form of particles having generally an average size range of 5 to 200 µm, preferably 10 to 100, even an average size range of 20 to 60 µm is possible.

The Ziegler-Natta catalyst (ZN-C) is preferably used in association with an alkyl aluminum cocatalyst and optionally external donors.

As further component in the instant polymerization process an external donor (ED) is preferably present. Suitable external donors (ED) include certain silanes, ethers, esters, amines, ketones, heterocyclic compounds and blends of these. It is especially preferred to use a silane. It is most preferred to use silanes of the general formula



wherein R^a , R^b and R^c denote a hydrocarbon radical, in particular an alkyl or cycloalkyl group, and wherein p and q are numbers ranging from 0 to 3 with their sum $p + q$ being equal

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to or less than 3. R^a , R^b and R^c can be chosen independently from one another and can be the same or different. Specific examples of such silanes are (tert-butyl)₂Si(OCH₃)₂, (cyclohexyl)(methyl)Si(OCH₃)₂, (phenyl)₂Si(OCH₃)₂ and (cyclopentyl)₂Si(OCH₃)₂, or of general formula



wherein R^3 and R^4 can be the same or different and represent a hydrocarbon group having 1 to 12 carbon atoms.

R^3 and R^4 are independently selected from the group consisting of linear aliphatic
 10 hydrocarbon group having 1 to 12 carbon atoms, branched aliphatic hydrocarbon group having 1 to 12 carbon atoms and cyclic aliphatic hydrocarbon group having 1 to 12 carbon atoms. It is in particular preferred that R^3 and R^4 are independently selected from the group consisting of methyl, ethyl, n-propyl, n-butyl, octyl, decanyl, iso-propyl, iso-butyl, isopentyl, tert.-butyl, tert.-amyl, neopentyl, cyclopentyl, cyclohexyl, methylcyclopentyl and
 15 cycloheptyl.

More preferably both R^1 and R^2 are the same, yet more preferably both R^3 and R^4 are an ethyl group.

20 In addition to the Ziegler-Natta catalyst (ZN-C) and the optional external donor (ED) a co-catalyst can be used. The co-catalyst is preferably a compound of group 13 of the periodic table (IUPAC), e.g. organo aluminum, such as an aluminum compound, like aluminum alkyl, aluminum halide or aluminum alkyl halide compound. Accordingly in one specific embodiment the co-catalyst (Co) is a trialkylaluminium, like triethylaluminium (TEAL),
 25 dialkyl aluminium chloride or alkyl aluminium dichloride or mixtures thereof. In one specific embodiment the co-catalyst (Co) is triethylaluminium (TEAL).

Advantageously, the triethyl aluminium (TEAL) has a hydride content, expressed as AlH₃, of less than 1.0 wt% with respect to the triethyl aluminium (TEAL). More preferably, the
 30 hydride content is less than 0.5 wt%, and most preferably the hydride content is less than 0.1 wt%.

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Preferably the ratio between the co-catalyst (Co) and the external donor (ED) [Co/ED] and/or the ratio between the co-catalyst (Co) and the transition metal (TM) [Co/TM] should be carefully chosen.

5 Accordingly

(a) the mol-ratio of co-catalyst (Co) to external donor (ED) [Co/ED] must be in the range of 5 to 45, preferably is in the range of 5 to 35, more preferably is in the range of 5 to 25, still more preferably is in the range of 8 to 20; and optionally

(b) the mol-ratio of co-catalyst (Co) to titanium compound (TC) [Co/TC] must be in the
10 range of above 40 to 500, preferably is in the range of 50 to 300, still more preferably is in the range of 60 to 150.

In the following the present invention is further illustrated by means of examples.

15

EXAMPLES

1. Measuring methods

The following definitions of terms and determination methods apply for the above general description of the invention as well as to the below examples unless otherwise defined.

20 **Calculation** of comonomer content of the second propylene copolymer fraction (R-PP2):

$$\frac{C(PP) - w(PP1) \times C(PP1)}{w(PP2)} = C(PP2) \quad (I)$$

wherein

w(PP1) is the weight fraction [in wt.-%] of the first propylene copolymer fraction (R-PP1),

w(PP2) is the weight fraction [in wt.-%] of second propylene copolymer fraction (R-PP2),

25

C(PP1) is the comonomer content [in mol-%] of the first random propylene copolymer fraction (R-PP1),

C(PP) is the comonomer content [in mol-%] of the random propylene copolymer (R-PP),

30 C(PP2) is the calculated comonomer content [in mol-%] of the second random propylene copolymer fraction (R-PP2).

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MFR₂ (230 °C) is measured according to ISO 1133 (230 °C, 2.16 kg load).

Quantification of microstructure by NMR spectroscopy

Quantitative nuclear-magnetic resonance (NMR) spectroscopy was used to quantify the comonomer content and comonomer sequence distribution of the polymers. Quantitative
5 ¹³C{¹H} NMR spectra were recorded in the solution-state using a Bruker Advance III 400 NMR spectrometer operating at 400.15 and 100.62 MHz for ¹H and ¹³C respectively. All spectra were recorded using a ¹³C optimised 10 mm extended temperature probehead at 125°C using nitrogen gas for all pneumatics. Approximately 200 mg of material was dissolved in 3 ml of 1,2-tetrachloroethane-*d*₂ (TCE-*d*₂) along with chromium-(III)-
10 acetylacetonate (Cr(acac)₃) resulting in a 65 mM solution of relaxation agent in solvent (Singh, G., Kothari, A., Gupta, V., Polymer Testing 28 5 (2009), 475). To ensure a homogenous solution, after initial sample preparation in a heat block, the NMR tube was further heated in a rotatory oven for at least 1 hour. Upon insertion into the magnet the tube was spun at 10 Hz. This setup was chosen primarily for the high resolution and
15 quantitatively needed for accurate ethylene content quantification. Standard single-pulse excitation was employed without NOE, using an optimised tip angle, 1 s recycle delay and a bi-level WALTZ16 decoupling scheme (Zhou, Z., Kuemmerle, R., Qiu, X., Redwine, D., Cong, R., Taha, A., Baugh, D. Winniford, B., J. Mag. Reson. 187 (2007) 225; Busico, V., Carbonniere, P., Cipullo, R., Pellecchia, R., Severn, J., Talarico, G., Macromol. Rapid
20 Commun. 2007, 28, 1128). A total of 6144 (6k) transients were acquired per spectra. Quantitative ¹³C{¹H} NMR spectra were processed, integrated and relevant quantitative properties determined from the integrals using proprietary computer programs. All chemical shifts were indirectly referenced to the central methylene group of the ethylene block (EEE) at 30.00 ppm using the chemical shift of the solvent. This approach allowed comparable
25 referencing even when this structural unit was not present. Characteristic signals corresponding to the incorporation of ethylene were observed Cheng, H. N., Macromolecules 17 (1984), 1950).

With characteristic signals corresponding to 2,1 erythro regio defects observed (as described in L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 2000, 100 (4), 1253, in Cheng,
30 H. N., Macromolecules 1984, 17, 1950, and in W-J. Wang and S. Zhu, Macromolecules 2000, 33 1157) the correction for the influence of the regio defects on determined properties

was required. Characteristic signals corresponding to other types of regio defects were not observed.

The comonomer fraction was quantified using the method of Wang et. al. (Wang, W-J., Zhu, S., Macromolecules 33 (2000), 1157) through integration of multiple signals across the whole spectral region in the $^{13}\text{C}\{^1\text{H}\}$ spectra. This method was chosen for its robust nature and ability to account for the presence of regio-defects when needed. Integral regions were slightly adjusted to increase applicability across the whole range of encountered comonomer contents.

For systems where only isolated ethylene in PPEPP sequences was observed the method of Wang et. al. was modified to reduce the influence of non-zero integrals of sites that are known to not be present. This approach reduced the overestimation of ethylene content for such systems and was achieved by reduction of the number of sites used to determine the absolute ethylene content to:

$$E = 0.5(S\beta\beta + S\beta\gamma + S\beta\delta + 0.5(S\alpha\beta + S\alpha\gamma))$$

Through the use of this set of sites the corresponding integral equation becomes:

$$E = 0.5(I_H + I_G + 0.5(I_C + I_D))$$

using the same notation used in the article of Wang et. al. (Wang, W-J., Zhu, S., Macromolecules 33 (2000), 1157). Equations used for absolute propylene content were not modified.

The mole percent comonomer incorporation was calculated from the mole fraction:

$$E [\text{mol}\%] = 100 * fE$$

The weight percent comonomer incorporation was calculated from the mole fraction:

$$E [\text{wt}\%] = 100 * (fE * 28.06) / ((fE * 28.06) + ((1-fE) * 42.08))$$

The comonomer sequence distribution at the triad level was determined using the analysis method of Kakugo et al. (Kakugo, M., Naito, Y., Mizunuma, K., Miyatake, T. Macromolecules 15 (1982) 1150). This method was chosen for its robust nature and integration regions slightly adjusted to increase applicability to a wider range of comonomer contents.

The relative content of isolated to block ethylene incorporation was calculated from the triad sequence distribution using the following relationship (equation (I)):

$$I(E) = \frac{f_{PEP}}{(f_{EEE} + f_{PEE} + f_{PEP})} \times 100 \quad (I)$$

wherein

I(E) is the relative content of isolated to block ethylene sequences [in %];

fPEP is the mol fraction of propylene/ethylene/propylene sequences (PEP) in the sample;

fPEE is the mol fraction of propylene/ethylene/ethylene sequences (PEE) and of ethylene/ethylene/propylene sequences (EEP) in the sample;

5 fEEE is the mol fraction of ethylene/ethylene/ethylene sequences (EEE) in the sample

Bulk density, BD, is measured according ASTM D 1895

Particle Size Distribution, PSD

Coulter Counter LS 200 at room temperature with heptane as medium.

The xylene solubles (XCS, wt.-%): Content of xylene cold solubles (XCS) is determined at

10 25 °C according ISO 16152; first edition; 2005-07-01

Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (M_w/M_n)

are determined by Gel Permeation Chromatography (GPC) according to the following method:

15 The weight average molecular weight M_w and the polydispersity (M_w/M_n), wherein M_n is the number average molecular weight and M_w is the weight average molecular weight) is measured by a method based on ISO 16014-1:2003 and ISO 16014-4:2003. A Waters Alliance GPCV 2000 instrument, equipped with refractive index detector and online viscosimeter was used with 3 x TSK-gel columns (GMHXL-HT) from TosoHaas and 1,2,4-
20 trichlorobenzene (TCB, stabilized with 200 mg/L 2,6-Di tert butyl-4-methyl-phenol) as solvent at 145 °C and at a constant flow rate of 1 mL/min. 216.5 μ L of sample solution were injected per analysis. The column set was calibrated using relative calibration with 19 narrow MWD polystyrene (PS) standards in the range of 0.5 kg/mol to 11 500 kg/mol and a set of well characterized broad polypropylene standards. All samples were prepared by
25 dissolving 5 - 10 mg of polymer in 10 mL (at 160 °C) of stabilized TCB (same as mobile phase) and keeping for 3 hours with continuous shaking prior sampling in into the GPC instrument.

DSC analysis, melting temperature (T_m) and heat of fusion (H_f), crystallization

temperature (T_c) and heat of crystallization (H_c): measured with a TA Instrument Q2000

30 differential scanning calorimetry (DSC) on 5 to 7 mg samples. DSC is run according to ISO 11357 / part 3 / method C2 in a heat / cool / heat cycle with a scan rate of 10 °C/min in the temperature range of -30 to +225°C. Crystallization temperature and heat of crystallization

(H_c) are determined from the cooling step, while melting temperature and heat of fusion (H_f) are determined from the second heating step.

The glass transition temperature T_g is determined by dynamic mechanical analysis according to ISO 6721-7. The measurements are done in torsion mode on compression
5 moulded samples ($40 \times 10 \times 1 \text{ mm}^3$) between -100°C and $+150^\circ\text{C}$ with a heating rate of $2^\circ\text{C}/\text{min}$ and a frequency of 1 Hz.

Tensile modulus in machine and transverse direction were determined according to ISO 527-3 at 23°C on air cooled blown films with a thickness of $50 \mu\text{m}$ produced as indicated below. Testing was performed at a cross head speed of 1 mm/min.

10 **Dart-drop:** Impact Strength was determined on Dart-drop (g/50%). Dart-drop is measured using ISO 7765-1, method "A". A dart with a 38 mm diameter hemispherical head is dropped from a height of 0.66 m onto a film sample clamped over a hole. If the specimen fails, the weight of the dart is reduced and if it does not fail the weight is increased. At least
15 20 specimens are tested. The weight resulting in failure of 50% of the specimens is calculated and this provides the dart drop impact (DDI) value (g). The relative DDI (g/ m) is then calculated by dividing the DDI by the thickness of the film.

Relative total Penetration Energy:

The impact strength of films is determined by the "Dynatest" method according to ISO 7725-2 at 0°C on air cooled blown films with a thickness of $50 \mu\text{m}$ produced as indicated
20 below. The value "Wbreak" [J/mm] represents the relative total penetration energy per mm thickness that a film can absorb before it breaks divided by the film thickness. The higher this value, the tougher the material is.

Tear resistance (determined as Elmendorf tear (N)): Applies both for the measurement in machine direction and transverse direction. The tear strength is measured using the ISO
25 6383/2 method. The force required to propagate tearing across a film sample is measured using a pendulum device. The pendulum swings under gravity through an arc, tearing the specimen from pre-cut slit. The film sample is fixed on one side by the pendulum and on the other side by a stationary clamp. The tear resistance is the force required to tear the
30 specimen. The relative tear resistance (N/mm) is then calculated by dividing the tear resistance by the thickness of the film. Air cooled blown films with a thickness of $50 \mu\text{m}$ produced as indicated below were used for this test.

Transparency, haze and clarity were determined according to ASTM D1003-00 on air cooled blown films with a thickness of 50 µm produced as indicated below.

2. Examples

The catalyst used in the polymerization process for the propylene copolymer of the inventive example (IE1) was produced as follows:

Used chemicals:

20 % solution in toluene of butyl ethyl magnesium (Mg(Bu)(Et), BEM), provided by Chemtura

2-ethylhexanol, provided by Amphochem

10 3-Butoxy-2-propanol - (DOWANOL™ PnB), provided by Dow

bis(2-ethylhexyl)citraconate, provided by SynphaBase

TiCl₄, provided by Millenium Chemicals

Toluene, provided by Aspokem

Viscoplex® 1-254, provided by Evonik

15 Heptane, provided by Chevron

Preparation of a Mg complex

First a magnesium alkoxide solution was prepared by adding, with stirring (70 rpm), into 1 l kg of a 20 wt-% solution in toluene of butyl ethyl magnesium (Mg(Bu)(Et), BEM), a mixture of 4.7 kg of 2-ethylhexanol and 1.2 kg of butoxypropanol in a 20 l stainless steel reactor.

20 During the addition the reactor contents were maintained below 45 °C. After addition was completed, mixing (70 rpm) of the reaction mixture was continued at 60 °C for 30 minutes. After cooling to room temperature 2.3 kg of the donor bis(2-ethylhexyl)citraconate was added to the Mg-alkoxide solution keeping temperature below 25 °C. Mixing was continued for 15 minutes under stirring (70 rpm)

25 Preparation of solid catalyst component

20.3 kg of TiCl₄ and 1.1 kg of toluene were added into a 20 l stainless steel reactor. Under 350 rpm mixing and keeping the temperature at 0 °C, 14.5 kg of the Mg complex prepared in example 1 was added during 1.5 hours. 1.7 l of Viscoplex® 1-254 and 7.5 kg of heptane were added and after 1 hour mixing at 0 °C the temperature of the formed emulsion was raised to 90 °C within 1 hour. After 30 minutes mixing was stopped catalyst droplets were solidified and the formed catalyst particles were allowed to settle. After settling (1 hour), the supernatant liquid was siphoned away.

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Then the catalyst particles were washed with 45 kg of toluene at 90°C for 20 minutes followed by two heptane washes (30 kg, 15 min). During the first heptane wash the temperature was decreased to 50 °C and during the second wash to room temperature.

The solid catalyst component was used along with triethyl-aluminium (TEAL) as co-catalyst
5 and dicyclo pentyl dimethoxy silane (D-donor) as donor.

CE1 is the commercial grade Borpure RB501BF available from Borealis Polyolefine GmbH, Austria, a propylene-ethylene random copolymer having a melting point of 140°C and an MFR₂ (230 °C) of 1.9 g/10min. CE2 is the commercial grade Borclear RB709CF available from Borealis Polyolefine GmbH, Austria, an α -nucleated propylene-ethylene random

10 copolymer having a melting point of 140°C and an MFR₂ (230 °C) of 1.5 g/10min.

The aluminium to donor ratio, the aluminium to titanium ratio and the polymerization conditions are indicated in table 1.

Table 1a: Preparation of the Examples

		IE1	CE1	CE2
TEAL/Ti	[mol/mol]	73		
TEAL/Donor	[mol/mol]	10		
Loop (R-PP1)				
Time	[h]	0.5		
Temperature	[°C]	70		
MFR ₂	[g/10min]	2.0		
XCS	[wt.-%]	9.2		
C2 content	[mol-%]	5.0		
H ₂ /C3 ratio	[mol/kmol]	0.39		
C2/C3 ratio	[mol/kmol]	7.3		
amount	[wt.-%]	40		
1 GPR (R-PP2)				
Time	[h]	3.1		
Temperature	[°C]	85		
MFR ₂	[g/10min]	2.0		
C2 content	[mol-%]	11.1		
H ₂ /C3 ratio	[mol/kmol]	4.6		
C2/C3 ratio	[mol/kmol]	37.3		
amount	[wt.-%]	60		
Final				
MFR ₂	[g/10min]	2.0	1.9	1.5
C2 content	[mol-%]	8.7	6.2	8.5
XCS	[wt.-%]	19.8	8.5	11.5
T _m	[°C]	140	140	140*
T _c	[°C]	105**	97	111
M _w	[kg/mol]	292		348
M _w /M _n	[-]	4.0	4.5	4.0
2,1	[%]	n.d.	n.d.	n.d.
T _g below -20 °C	[°C]	n.d.	n.d.	n.d.
T _g above -20 °C	[°C]	-4.6	-6.0	-8.0

n.d. not detectable

* 2nd T_m at 124°C** T_c of IE2 (nucleated) 119°C

5

The films for the examples are produced on a Windmöller & Hölscher (W&H) monolayer blown film line (W & H Varex 60).

Extruder: Varex E 60.30D, cylinder diameter 60mm, screw length to diameter ratio of 30, 4 heated and 3 cooled zones

10 Blown film die diameter: 200 mm

Die gap: 0.8-1.2 mm

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Extruder temperatures: 230 °C

Die temperature: 220 °C

Throughput: 60 kg/h

Melt temperature, melt pressure & screw speed: see table 2

5 BUR: 2.5

Frost line height: 700 mm

Take off speed: 14.2 m/min

Table 2: Properties of the Examples

		IE1	IE2 ¹⁾	CE1	CE2
melt pressure	[bar]	88	88	121	149
screw speed	[1/min]	50	50	70	50
melt temperature	[°C]	238	238	238	238
film thickness	[µm]	50	52	50	50
transparency	[%]	94	93	94	94
haze	[%]	12	9	23	4
clarity	[%]	94	93	85	97
tensile modulus MD	[MPa]	484	545	788	800
tensile modulus TD	[MPa]	472	538	808	750
DDI	[F50/g]	268	143	57	70
tear resistance MD	[N/mm]	7.6	5.6	6.0	4.8
tear resistance TD	[N/mm]	14.7	9.4	9.0	10.3
Dyna (23 °C)	[J/mm]	11.7	8.6	-	6.0

10 ¹⁾ is inventive example 1 containing 2000 ppm Millad 3988i, i.e. an α -nucleating agent based on a sorbitol derivative

Table 3: Relative content of isolated to block ethylene sequences (I(E))

		IE1	IE2	CE1	CE2
I(E) ¹⁾	[%]	59.8	59.8	73.6	68.7
fEEE	[mol.-%]	1.19	1.19	0.6	0.69
fEEP	[mol.-%]	2.34	2.34	1.05	2.04
fPEP	[mol.-%]	5.26	5.26	4.6	5.98
fPPP	[mol.-%]	79.76	79.76	83.56	76.63
fEPP	[mol.-%]	10.73	10.73	9.49	11.22
fEPE	[mol.-%]	0.73	0.73	0.69	0.67

$$1) \quad I(E) = \frac{f_{PEP}}{(f_{EEE} + f_{PEE} + f_{PEP})} \times 100(I)$$

CLAIMS

1. Propylene copolymer (R-PP) having

- 5 (a) a comonomer content in the range of 2.5 to 11.5 mol.-%;
- (b) a melt flow rate MFR2 (230 °C) measured according to ISO 1133 in the range of 1.0 to 16.0 g/10min; and
- (c) a relative content of isolated to block ethylene sequences (I(E)) in the range of 45.0 to 69.0 %, wherein the I(E) content is defined by equation (I)

$$I(E) = \frac{f_{PEP}}{(f_{EEE} + f_{PEE} + f_{PEP})} \times 100 \quad (I)$$

10 wherein

I(E) is the relative content of isolated to block ethylene sequences [in %];

fPEP is the mol fraction of propylene/ethylene/propylene sequences (PEP) in the sample;

fPEE is the mol fraction of propylene/ethylene/ethylene sequences (PEE)

15 and of ethylene/ethylene/propylene sequences (EEP) in the sample;

fEEE is the mol fraction of ethylene/ethylene/ethylene sequences (EEE) in the sample

wherein all sequence concentrations being based on a statistical triad analysis of ¹³C-NMR data.

20

2. Propylene copolymer (R-PP) according to claim 1, wherein said propylene copolymer (R-PP) has a xylene cold soluble fraction (XCS) in the range of 4.0 to 25.0 wt.-%.

- 25 3. Propylene copolymer (R-PP) according to claim 1 or 2, wherein said propylene copolymer (R-PP) has

- (a) a glass transition temperature in the range of -12 to +2 °C;
- and/or
- (b) no glass transition temperature below -20 °C.

30

4. Propylene copolymer (R-PP) according to any one of the preceding claims, wherein wherein said propylene copolymer (R-PP) has

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- (a) a melting temperature in the range of 135 to 155 °C;
and/or
(b) a crystallization temperature in the range of 99 to 110 °C.
- 5 5. Propylene copolymer (R-PP) according to any one of the preceding claims, wherein
wherein said propylene copolymer (R-PP) has
(a) has 2,1 regio-defects of at most 0.4 % determined by ¹³C-NMR
spectroscopy;
and/or
10 (b) is monophasic.
6. Propylene copolymer (R-PP) according to any one of the preceding claims, wherein
wherein the comonomer is selected from ethylene, C₄ to C₁₂ α-olefin, and mixtures
thereof, preferably the comonomer is ethylene.
- 15 7. Propylene copolymer (R-PP) according to any one of the preceding claims, wherein
said propylene copolymer (R-PP) comprises two fractions, a first propylene
copolymer fraction (R-PP1) and a second propylene copolymer fraction (R-PP2),
said first propylene copolymer fraction (R-PP1) differs from said second propylene
20 copolymer fraction (R-PP2) in the comonomer content.
8. Propylene copolymer (R-PP) according to claim 7, wherein
(a) the weight ratio between the first propylene copolymer fraction (R-PP1) and
the second propylene copolymer fraction (R-PP2) [(R-PP1):(R-PP2)] is
25 70:30 to 30:70;
and/or
(b) the comonomers for the first propylene copolymer fraction (R-PP1) and the
second propylene copolymer fraction (R-PP2) are selected from ethylene, C₄
to C₁₂ α-olefin, and mixtures thereof, preferably the comonomers for the
30 first propylene copolymer fraction (R-PP1) and the second propylene
copolymer fraction (R-PP2) are the same and are selected from ethylene, C₄
to C₁₂ α-olefin, and mixtures thereof.

9. Propylene copolymer (R-PP) according to claim 7 or 8, wherein
- (a) the first propylene copolymer fraction (R-PP1) is the comonomer lean fraction and the second propylene copolymer fraction (R-PP2) is the comonomer rich fraction
- 5 and/or
- (b) the first propylene copolymer fraction (R-PP1) has a lower comonomer content than the propylene copolymer (R-PP).
10. Propylene copolymer (R-PP) to any one of the preceding claims 7 to 9, wherein
- (a) the first propylene copolymer fraction (R-PP1) has a comonomer content in the range of 1.0 to 6.5 mol-% based on the first propylene copolymer fraction (R-PP1);
- and/or, preferably and,
- 15 (b) the second propylene copolymer fraction (R-PP2) has a comonomer content in the range of more than 7.0 to 15.0 mol-% based on the second propylene copolymer fraction (R-PP2).
11. Propylene copolymer (R-PP) according to any one of the preceding claims 7 to 10, wherein
- 20 (a) the first random propylene copolymer fraction (R-PP1) and the second random propylene copolymer fraction (R-PP2) fulfill together the in-equation (III)
- $$\frac{Co(R-PP2)}{Co(R-PP1)} \geq 1.0 \quad (III);$$
- 25 wherein
- Co (R-PP1) is the comonomer content [mol.-%] of the first propylene copolymer fraction (R-PP1),
- Co (R-PP2) is the comonomer content [mol.-%] of the second propylene copolymer fraction (R-PP2).
- 30 and/or,
- (b) the first random propylene copolymer fraction (R-PP1) and the random propylene copolymer fraction (R-PP) fulfill together the in-equation (IV)

- 40 -

$$\frac{Co(R-PP)}{Co(R-PP1)} \geq 1.0 \quad (IV)$$

wherein

Co (R-PP1) is the comonomer content [mol.-%] of the first propylene copolymer fraction (R-PP1),

5 Co (R-PP) is the comonomer content [mol.-%] of the propylene copolymer (R-PP).

12. Unoriented film comprising a propylene copolymer to any one of the preceding claims 1 to 11.

10

13. Unoriented film according to claim 12, wherein the film is a cast film or a blown film, like air cooled blown film.

14. Process for producing a propylene copolymer (R-PP) according to any one of the preceding claims 1 to 11, wherein the propylene copolymer (R-PP) has been produced in the presence of

15

- (a) a Ziegler-Natta catalyst (ZN-C) comprises a titanium compound (TC), a magnesium compound (MC) and an internal donor (ID), wherein said internal donor (ID) is a non-phthalic acid ester,
- (b) optionally a co-catalyst (Co), and
- (c) optionally an external donor (ED).

20

15. Process according to claim 14, wherein

- (a) the internal donor (ID) is selected from optionally substituted malonates, maleates, succinates, glutarates, cyclohexene-1,2-dicarboxylates, benzoates and derivatives and/or mixtures thereof, preferably the internal donor (ID) is a citraconate;
- (b) the molar-ratio of co-catalyst (Co) to external donor (ED) [Co/ED] is 5 to 45.

25

30

16. Process according to claim 14 or 15, wherein the propylene copolymer (R-PP) is produced in a sequential polymerization process comprising at least two reactors

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(R1) and (R2), in the first reactor (R1) the first propylene copolymer fraction (R-PP1) is produced and subsequently transferred into the second reactor (R2), in the second reactor (R2) the second propylene copolymer fraction (R-PP2) is produced in the presence of the first propylene copolymer fraction (R-PP1).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/059592

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F210/06 C08L23/14 C08J5/18
ADD.

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 C08L C08J

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 386 604 A1 (BOREALIS AG [AT]) 16 November 2011 (2011-11-16) paragraphs [0023], [0100]; claims 1-7 -----	1,2,4-11
X	EP 2 065 407 A1 (BOREALIS TECH OY [FI]) 3 June 2009 (2009-06-03) paragraph [0003]; claims 1,2,4-6,12,13; examples 4,5; table 2 -----	1,2,4-12
X	EP 2 251 361 A1 (BOREALIS AG [AT]) 17 November 2010 (2010-11-17) paragraph [0061]; examples 5-7; tables 2A,2B -----	1,2,5-7, 12
X,P	EP 2 610 274 A1 (BOREALIS AG [AT]) 3 July 2013 (2013-07-03) paragraph [0004]; claims 1-4; example 3 -----	1,2,5,6, 14-16



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/059592

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