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(54) **Polypropylene with narrow molecular weight distribution and process for preparation thereof.**

(57) The present invention relates to a polypropylene with narrow molecular weight distribution and a process for preparing the same, and particularly relates to a propylene polymer with narrow molecular weight distribution which is directly prepared by polymerization in a reactor using a Ziegler-Natta catalyst. The polymer is featured with relatively high and adjustable isotacticity, narrow molecular weight distribution and high polydispersity index of high-molecular-weight tail, and is free of regio-irregularity of propylene, and has relatively high melting point and crystallization temperature. In comparison with narrow molecular-weight-distribution polypropylene produced by conventional degradation process, it has advantages in cost, energy saving and environmental protection and the like. The product of the present invention is particularly suitable for use in applications with relatively high requirement on fluidity such as spinning, thin-wall injecting, and casting processes, and preparation of transparent materials. In addition, due to narrow molecular weight distribution, the polymer of the present invention also has advantages in applications relating to transparency.

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Polypropylene with narrow molecular weight distribution and process for preparation thereof

Technical Field

The present invention relates to a polypropylene with narrow molecular weight distribution and a process for preparing the same, and particularly relates to a polypropylene with narrow molecular weight distribution which is directly prepared by polymerization in reactors using a Ziegler-Natta catalyst.

Background Art

Molecular weight distribution width of polypropylene is an important structural parameter, and directly influences processing behavior and physical and mechanical properties of polypropylene. Polypropylene with narrow molecular weight distribution has a wider Newton plateau zone during the flowing, less change of viscosity with fluctuation of shear rate, and it is easier to stably control extrusion amount, and it is particularly suitable for molding processes requiring low viscosity and high fluidity. For example, in the aspect of applications such as spinning, the molecular weight distribution of polypropylene need to be controlled as narrow as possible to improve nozzle pressure stability and to ensure uniformity of fineness of filaments; in the aspect of high-fluidity injection molding, a narrow molecular weight distribution facilitates reducing the warpage of articles and improving the impact behavior of articles; in case that a clarifier is not added, a narrow molecular weight distribution also helps to improve transparency of samples and reduce the haze. In the industry, a process for preparing polypropylene with narrow molecular weight distribution is usually degradation by adding an peroxide (so-called "controlled rheology polypropylene"), but the use of peroxide increases the cost of products, and at the same time

the residual peroxide also readily causes odor in finished articles which limits their application in some fields.

Disclosure of the Invention

The inventors found by studying that using a Ziegler-Natta catalyst, a polymer of propylene with a narrow molecular weight distribution can be directly prepared by polymerization in reactors.

Hence, the first object of the present invention is to provide a polypropylene with a narrow molecular weight distribution. The preparation of the polypropylene with narrow molecular weight distribution according to the present invention does not use a peroxide, which reduces cost, and the product has no abnormal odor, and has a higher crystallization temperature in comparison with polypropylenes with narrow molecular weight distribution obtained by degradation process, which indicates that it has higher crystallization rate, and facilitates shortening molding processing cycle and increasing molding efficiency. Further, the polypropylene with narrow molecular weight distribution as provided by the present invention has relatively high and adjustable isotacticity, relatively high melting point and crystallization temperature, better cost performance and wider applications.

The narrow molecular-weight-distribution polypropylene of the present invention has a molecular weight distribution index (polydispersity index), Mw/Mn, of 2.5 to 5.5, preferably 3.0 to 4.9; and a polydispersity index of high-molecular weight tail in molecular weight distribution width, PI_{HT}, of greater than 1.9, preferably greater than 2.1. The polydispersity index of high-molecular weight tail, PI_{HT}, is one of important features of the narrow molecular-weight-distribution polypropylene of the present invention to be distinguished from narrow molecular-weight-distribution polypropylene obtained by

peroxide degradation, and higher PI_{HT} means a more significant high molecular weight tail existing in polypropylene, while the high molecular weight tail can preferentially form nuclei during the crystallization, so that the polypropylene has an increased crystallization temperature and an accelerated crystallization, which helps to shorten molding process cycle and increase molding efficiency.

The narrow molecular-weight-distribution polypropylene of the present invention has isotactic pentad [mmmm] sequences in an amount of greater than 85%, preferably greater than 90%, more preferably greater than 93%.

The narrow molecular-weight-distribution polypropylene of the present invention is free of regio-irregularity caused by 2,1-insertion and 1,3-insertion of propylene. For polypropylenes with the same isotacticity in general sense, the existence of regio-irregularity will result in a declined melting point of samples, and in turn affect performances thereof, for example, service temperature.

The narrow molecular-weight-distribution polypropylene of the present invention has a crystallization temperature, Tc, of higher than 113°C, preferably higher than 115°C.

The narrow molecular-weight-distribution polypropylene of the present invention has a xylene-soluble fraction of less than 4.4 wt%, preferably less than 2.3 wt%, more preferably less than 1.6 wt%. In general sense, the lower the xylene-soluble fraction is, the higher the isotacticity of the material is, and thus the better the rigidity and the heat resistance are. In addition, for some materials contacting foods, drugs or solvents, the xylene-soluble fraction is low, the contents of migrated, or dissolved or extracted substances are low, and their applications are more safe and more reliable.

The polypropylene of the present invention, based on narrow molecular weight distribution, has a melt flow rate, MFR, ranging

from 0.01 to 1000 g/10min, preferably from 1 to 1000 g/10min, more preferably from 1 to 399 g/10min, particularly preferably from 10 to 100 g/10min. It is generally assumed that the introduction of a chain transfer agent during the polymerization would result in narrowing of molecular weight distribution of the polymer. In the polymerization of propylene, hydrogen gas is usually introduced as chain transfer agent to regulate molecular weight and melt flow rate of the polymer, the higher the concentration of hydrogen gas is, the lower the molecular weight of the obtained product is, and the higher the melt flow rate is. It is proposed in some researches that for some high performance catalysts for polypropylene, the molecular weight distribution width of the obtained products is inversely proportional to the concentration of added hydrogen gas. This means that in order to control the same narrow molecular weight distribution, it is more difficult for a sample with low melt flow rate than a sample with high melt flow rate. The present invention can meet both of requirements for melt flow rate and for narrow molecular weight distribution of polypropylene, to adapt requirements for processing and application of materials.

The narrow molecular-weight-distribution polypropylene of the present invention is directly prepared by polymerization in reactors, and has both narrow molecular weight distribution and high polydispersity index of high-molecular-weight tail, PI_{HT}.

The second object of the present invention is to provide a process for preparing the narrow molecular-weight-distribution polypropylene of the present invention, comprising:

(1) pre-polymerizing propylene in the presence of a Ziegler-Natta catalyst,

(2) polymerizing propylene in the presence of a prepolymer of propylene obtained in step (1).

Specifically, it comprises the following steps:

(1) pre-polymerizing propylene in the presence of a Ziegler-Natta catalyst, in a gas phase or a liquid phase, at -10°C to 50°C, and 0.1 to 10.0 MPa to obtain a prepolymer of propylene, wherein the pre-polymerization times is controlled as 2 to 3000 g polymer/g catalyst, preferably 3 to 2000 g polymer/g catalyst;

(2) homopolymerizing propylene in the presence of the prepolymer of propylene obtained in step (1), in a gas phase or a liquid phase, at 91 to 150°C, preferably 91 to 110°C, and 1.0 to 6.0 MPa, for the polymerization time of 0.5 to 4.0 h, to obtain the propylene polymer.

The above step (1) and step (2) of the present invention can be performed discontinuously in the same one reactor, and can also be performed continuously in different reactors.

In the process of the present invention, in the step (1), the pre-polymerization temperature is controlled at -10°C to 50°C, preferably 0 to 30°C, more preferably 10 to 25°C. The pre-polymerization pressure is 0.1 to 10.0 MPa, preferably 1.0 to 6.0 MPa, more preferably 1.5 to 5.5 MPa. The pre-polymerization is preferably performed in liquid phase, and specifically can be selected as liquid phase bulk pre-polymerization of propylene. The pre-polymerization times is controlled as 2 to 3000 g polymer/g catalyst, preferably 3 to 2000 g polymer/g catalyst, more preferably 3 to 1000 g polymer/g catalyst.

In the present invention, the term "pre-polymerization times" refers to a ratio of the weight of prepolymer to the weight of catalyst as originally added. Generally, for batch pre-polymerization, pre-polymerization times can be determined by directly measuring the weight of prepolymer and dividing it by the weight of added catalyst; for continuous pre-polymerization, pre-polymerization times is usually indirectly controlled by regulating resident time of the

reaction and polymerization temperature. For different catalysts, different polymerization temperatures, different polymerization modes (gas phase, liquid phase bulk, etc.) and different polymerization pressures, even if the pre-polymerization retention time is the same, the pre-polymerization times is also different, and could be obtained by integral calculation according to reaction kinetic curve of the catalyst.

In the process of the present invention, the polymerization in step (2) is performed in the presence of the prepolymer obtained in step (1), polymerization temperature is 91 to 150°C, preferably 91 to 110°C, and polymerization pressure is 1.0 to 6.0 MPa. It can be performed in either gas phase or liquid phase, and preferably it is a gas phase polymerization process. Specifically, it can be performed in a gas-phase horizontal reactor, which reactor has horizontal mixer shaft and quenching liquid for removing heat, has the stirring speed of 10 to 150 rpm and mixing blades whose types are selected from T type, rectangle, inclined paddles, door type, wedge-shaped and any combination thereof. The polymerization time or resident time can be controlled within 0.5 to 4.0 h. The melt flow rate of the polymer can be regulated with a molecular weight regulator (generally, H_2). The MFR of the obtained polymer can be controlled as 0.01 to 1000 g/10min, preferably 1 to 1000 g/10min, preferably 1 to 399 g/10min, more preferably 10 to 100 g/10min.

By changing the polymerization temperature in step (2), a polypropylene product with high stereo-regularity (tacticity) can be obtained in controlled manner and narrow molecular weight distribution can be achieved.

In the process of the present invention, the Ziegler-Natta catalyst can be selected from Ziegler-Natta catalysts known in the art, preferably including a reaction production of the following components:

(1) a titanium-containing solid catalyst component;

(2) an alkyl aluminum compound;

preferably, further comprising (3) an external electron donor compound.

The titanium-containing solid catalyst component of the component (1) is a reaction product of contacting an alkoxy magnesium compound, a titanium compound and an internal electron donor compound.

The titanium compound is selected from at least one compound of Formula (I):

$$Ti(OR)_{4-n}X_n \qquad (I)$$

in which

R is selected from C_1-C_{14} aliphatic hydrocarbonyl or aromatic hydrocarbonyl,

X is halogen atom,

n is an integer selected from 0 to 4; when n is equal to or less than 2, the R groups present can be the same or different.

The halogen atom can be chlorine, bromine or iodine. Specifically, the titanium compound is selected from at least one of tetraalkoxy titanium, titanium tetrahalide, alkoxy titanium trihalide, dialkoxy titanium dihalide and trialkoxy titanium monohalide. More specifically, the tetraalkoxy titanium is selected from at least one of tetramethoxy titanium, tetraethoxy titanium, tetra-n-propoxy titanium, tetra-iso-propoxy titanium, tetra-n-butoxy titanium, tetra-iso-butoxy titanium, tetra-cyclohexyloxy titanium, tetraphenoxy titanium; the titanium tetrahalide is selected from at least one of titanium tetrachloride, titanium tetrabromide, titanium tetraiodide; the alkoxy titanium trihalide is selected from at least one of methoxy titanium trichloride, ethoxy titanium trichloride, propoxy titanium trichloride, n-butoxy titanium trichloride, ethoxy

titanium tribromide; the dialkoxy titanium dihalide is selected from at least one of dimethoxy titanium dichloride, diethoxy titanium dichloride, di-n-propoxy titanium dichloride, di-iso-propoxy titanium dichloride, diethoxy titanium dibromide; the trialkoxy titanium monohalide is selected from at least one of trimethoxy titanium monochloride, triethoxy titanium monochloride, tri-n-propoxy titanium monochloride, tri-iso-propoxy titanium monochloride; the titanium tetrahalide compound is preferred, and titanium tetrachloride is particularly preferred.

The alkoxy magnesium compound is selected from at least one of the compounds of Formula (II):

$$Mg(OR^1)_{2-m}(OR^2)_m \qquad (II)$$

wherein R^1 and R^2 are the same or different, and each are selected from one of C_1-C_8 linear or branched alkyl groups, $0 \leq m \leq 2$. Preferably, R^1 and R^2 each are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, n-hexyl, (2-ethyl)hexyl; more preferably, R^1 is ethyl, R^2 is (2-ethyl)hexyl, $0.001 \leq m \leq 0.5$, preferably $0.001 \leq m \leq 0.25$, more preferably $0.001 \leq m \leq 0.1$. It is particularly pointed out that the alkoxy magnesium represented by the formula merely shows compositional contents of various alkoxy groups, i.e., molar ratios, but does not completely represent specific structure of alkoxy magnesium. Specifically, for example, Mg(OEt)(OiPr) merely shows that the molar ratio of ethoxy to isopropoxy in alkoxy magnesium compound is 1, that is, it can be either a mixture of diethoxy magnesium and diisopropoxy magnesium with a molar ratio of 1, or ethoxyisopropoxy magnesium compound, or a mixture of these three compounds; it can be a mixture consisting of alkoxy magnesium compounds with several structures in which the total molar ratio of ethoxy to

isopropoxy is 1. Herein, Et represents ethyl, iPr represents isopropyl.

The alkoxy magnesium compound has sphere-like appearance, average particle size (D50) of 10 to 150μm, preferably 15 to 100 μm, more preferably 18 to 80 μm, and particle size distribution index SPAN<1.1, preferably particle size distribution index SPAN<1.05, wherein SPAN is calculated by following formula (III):

$$\mathbf{SPAN= (D90-D10)/D50 \quad (III)}$$

In the Formula (III), D90 represents a particle diameter corresponding to an accumulation weight fraction of 90%, D10 represents a particle diameter corresponding to an accumulation weight fraction of 10%, and D50 represents a particle diameter corresponding to an accumulation weight fraction of 50%.

The alkoxy magnesium compound according to the present invention may contain a trace of magnesium halides (for example, MgI_2 or $MgCl_2$) or alcoholates thereof, but its purity should be greater than 90%, preferably greater than 95%, more preferably above 98%, expressed as the content of magnesium compound of Formula (II).

The alkoxy magnesium compound according to the present invention is prepared by reaction of magnesium metal, alcohol (R^1OH, R^2OH) corresponding to the alkoxy groups and a mixed halogenating agent in an atmosphere of inert gas. Herein, the molar ratio of magnesium metal to halogen atom in the mixed halogenating agent is 1:0.0002 to 1:0.2, preferably 1:0.001 to 1:0.08; the weight ratio of alcohol to magnesium is 4:1 to 50:1, preferably 6:1 to 25:1, wherein the molar ratio x of R^1OH to R^2OH is $3(2-m)/m>x>(2-m)/m$. The reaction temperature is 30 to 90°C, preferably 30 to 80°C, more preferably 50 to 75°C. The reaction time is 2 to 30 h. In the practical operation, the end of reaction

can be determined by observing the end of the release of hydrogen gas generated during the reaction.

For the preparation of the alkoxy magnesium according to the present invention, the water content of the alcohol is not particularly limited, while the water content should be as little as possible in order that the obtained alkoxy magnesium could have better performance. The water content in the alcohol is generally controlled as 1000 ppm or less, preferably 200 ppm or less. In the present invention, the magnesium as used is magnesium metal, and in case that it has good reactivity, its shape is not particularly limited, and can be for example, in granule, riband or powder shape. The magnesium metal is preferably sphere-like particle with average particle size of 10 to 360 μm, more preferably 50 to 300 μm, in order to keep the average particle size of the generated alkoxy magnesium within a suitable range and make the particle have good morphology. In addition, the surface of magnesium metal is not particularly limited, but coated film of hydroxides and the like formed on the surface of magnesium metal may slow down the reaction, so the total content of active magnesium is preferably >95%, more preferably >98%.

The mixed halogenating agent can be a combination of halogen and halogen compound, and the halogen and the halogen compound are selected from but not limited to: iodine, bromine, chlorine, magnesium chloride, magnesium bromide, magnesium iodide, potassium chloride, potassium bromide, potassium iodide, calcium chloride, calcium bromide, calcium iodide, mercuric chloride, mercuric bromide, mercuric iodide, ethoxy magnesium iodide, methoxy magnesium iodide, isopropyl magnesium iodide, hydrogen chloride, chloroacetyl chloride, etc. The mixed halogenating agent is preferably a combination of iodine and magnesium chloride. The weight ratio of iodine to magnesium chloride is preferably 1:0.02 to 1:20, more preferably 1:0.1 to 1:10.

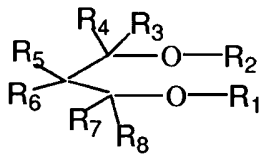
The inert gas atmosphere is preferably nitrogen gas atmosphere, argon gas atmosphere.

For the preparation of the alkoxy magnesium compound according to the present invention, the manner of adding the halogenating agent is not particularly limited, and it can be dissolved in an alcohol and then added, or can be directly added in solid or liquid form to magnesium metal and alcohol, or can be added dropwise to an alcoholic solution of the halogenating agent during the heating of magnesium metal and the alcoholic solution, thereby to perform the reaction for preparing the alkoxy magnesium compound as a carrier.

For the preparation of the alkoxy magnesium compound according to the present invention, magnesium metal, alcohol, halogenating agent and inert solvent can be initially added once, or added in batches. If the starting materials are added in batches, transient generation of a large amount of hydrogen gas can be prevented, and a mist of alcohol or halogenating agent caused by the transient generation of a large amount of hydrogen gas can be prevented, so such adding manner is preferred in view of safety and reaction uniformity. The number of batches can be determined according to the size of the reactor and the amounts of various materials. After the end of reaction, the obtained final product, dialkoxy magnesium, can be dried and stored, or can be suspended in an inert diluent used for preparing the catalyst solid component in the next step.

During the preparation, an inert organic solvent can be selectively used, and can be selected from at least one of C_6 to C_{10} alkanes or aromatics, preferably hexane, heptane, octane, decane, benzene, toluene, xylene or derivatives thereof, etc.

The internal electron donor compound is selected from at least one of diether compounds of Formula (IV),



(IV)

in which

R_1 and R_2 are the same or different, and each independently selected from C_1-C_{20} linear, branched and cyclic aliphatic groups,

R_3, R_4, R_5, R_6, R_7 and R_8 are the same or different, and each independently selected from hydrogen, halogen atom and linear or branched C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl and C_7-C_{20} arylalkyl, optionally, R_3 to R_8 can be bonded to each other to form a ring.

Preferably, R_1 and R_2 are the same or different, and each independently selected from C_1-C_6 linear or branched alkyl; R_5 and R_6 are the same or different, and each independently selected from linear or branched C_1-C_{10} alkyl, or C_3-C_{10} cycloalkyl.

Specific compounds are as follows: 2-isopropyl-2-isopentyl-1,3-dimethoxypropane, 9,9-di(methoxymethyl)fluorene, 2-isobutyl-2-isopropyl-1,3-dimethoxypropane, 2,2-dicyclopentyldimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2-isobutyl-2-isopropyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, etc.

For the preparation of the catalyst solid component according to the present invention, the molar ratio of the used amount of the titanium compound to the magnesium in the alkoxy magnesium compound can be (0.5 to 100):1, preferably (1 to 50):1.

For the preparation of the catalyst solid component according to the present invention, the molar ratio of the amount of the internal electron donor compound to the magnesium in the alkoxy magnesium compound can be (0.005 to 10):1, preferably (0.01 to 1):1.

For the preparation of the catalyst solid component of the present invention, alkoxy magnesium compound, internal electron donor compound and titanium compound can contact and react in any manner to prepare the catalyst solid component. For example, it can be prepared via the following methods:

Method 1:

1. The alkoxy magnesium carrier, the internal electron donor and an inert diluent are formulated into a suspension, then reacted with a mixture formed from the titanium compound and an inert diluent, and filtered;
2. The obtained solid is added to a mixture of the titanium compound and an inert diluent for further reaction, and filtered;
3. The reaction of step 2 is repeated for 2 to 4 times;
4. The above solid is washed with an inert solvent to obtain the catalyst solid component.

Method 2:

1. The alkoxy magnesium carrier, a part of the internal electron donor and an inert diluent are formulated into a suspension, then reacted with a mixture formed from the titanium compound and an inert diluent, and filtered;
2. The obtained solid is added to a mixture of the titanium compound, an inert diluent and the remaining internal electron donor for further reaction, and filtered;
3. The obtained solid is further added to a mixture of the titanium compound and an inert diluent for further reaction, and filtered;
4. The reaction of step 3 is repeated for 2 to 4 times;
5. The above solid is washed with an inert solvent to obtain the catalyst solid component.

Method 3:

1. The alkoxy magnesium carrier and an inert diluent are formulated into a suspension, then subjected to reaction

with a mixture formed from the titanium compound and an inert diluent, added with the electron donor compound for further reaction, and filtered;

2. The obtained solid is added to a mixture of the titanium compound and an inert diluent for further reaction, and filtered;
3. The reaction of step 2 is repeated for 2 to 4 times;
4. The above solid is washed with an inert solvent to obtain the catalyst solid component.

Method 4:

1. The alkoxy magnesium carrier, a part of the internal electron donor and an inert diluent are formulated into a suspension, then subjected to reaction with a mixture formed from the titanium compound and an inert diluent, added with the remaining electron donor compounds for further reaction, and filtered;
2. The obtained solid is added to a mixture of the titanium compound and an inert diluent for further reaction, and filtered;
3. The reaction of step 2 is repeated for 2 to 4 times;
4. The above solid is washed with an inert solvent to obtain the catalyst solid component.

For the preparation of the catalyst solid component according to the present invention, the molar ratio of the amount of the inert diluent to the magnesium in alkoxy magnesium compound can be (0.5 to 100):1, preferably (1 to 50):1. The inert diluent is preferably toluene.

For the preparation of the catalyst solid component according to the present invention, the alkoxy magnesium carrier, the internal electron donor compound, the inert diluent and the titanium compound are preferably subjected to reaction under the following conditions: reaction temperature of -40 to 200°C,

preferably -20 to 150°C; reaction time of 1 minute to 20 hours, preferably 5 minutes to 8 hours.

For the preparation of the catalyst solid component according to the present invention, the order of adding the alkoxy magnesium carrier, the internal electron donor compound, the inert diluent and the titanium compound is not particularly limited, for example, these components can be mixed in the presence of the inert diluent, or they can be diluted with the inert diluent beforehand and then mixed. The times of mixing are not particularly limited, either, and the mixing can be performed once, or for several times.

For the preparation of the catalyst solid component according to the present invention, the inert solvent for washing is preferably hexane. The washing method is not particularly limited, and preferably can be decantation, filtration, etc. There is no specific limitation on used amount of inert solvent, washing time, washing times. For the compound corresponding to 1 mol magnesium, the solvent is usually used in an amount of 1 to 1000 mol, preferably 10 to 500 mol, and the washing is usually performed for 1 to 24 h, preferably 6 to 10 h. In addition, in view of uniformity and efficiency of washing, stirring is preferably carried out during the washing.

The component (2) of the catalyst according to the present invention is alkyl aluminum compound of Formula (V), in which R' is hydrogen or a hydrocarbonyl with 1 to 20 carbon atoms, X' is halogen, n' is an integer of 1 to 3; specifically, it can be selected from a group consisting of triethyl aluminum, tripropyl aluminum, tri-n-butyl aluminum, tri-iso-butyl aluminum, tri-n-octyl aluminum, diethyl aluminum monohydride, di-iso-butyl aluminum monohydride, diethyl aluminum monochloride, di-iso-butyl aluminum monochloride, ethyl aluminum sesquichloride, ethyl aluminum dichloride, preferably triethyl aluminum, tri-iso-butyl aluminum.

$$AlR'_{n'}X'_{3-n'} \qquad (V)$$

In the propylene polymerization catalyst according to the present invention, the external electron donor component can be all kinds of external electron donors as known in the art, and thus is not particularly limited. It is preferably organosilicon compound of Formula (VII),

$$R^{1''}_{m''}R^{2''}_{n''}Si(OR^{3''})_{4-m''-n''} \qquad (VII)$$

in which

$R^{1''}$ and $R^{2''}$ are the same or different, and each are one of halogen, hydrogen atom, alkyl with 1 to 20 carbon atoms, cycloalkyl with 3 to 20 carbon atoms, aryl with 6 to 20 carbon atoms and halogenated alkyl with 1 to 20 carbon atoms; $R^{3''}$ is one of alkyl with 1 to 20 carbon atoms, cycloalkyl with 3 to 20 carbon atoms, aryl with 6 to 20 carbon atoms and halogenated alkyl with 1 to 20 carbon atoms; m'' and n'' each are an integer of 0 to 3, and m''+ n''<4.

The specific examples of the organosilicon compound can be trimethylmethoxysilane, diisopropyldimethoxysilane, diisobutyldimethoxysilane, isopropylisobutyldimethoxysilane, di-tert-butyldimethoxysilane, tert-butylmethyldimethoxysilane, tert-butylethyldimethoxysilane, tert-butyl- propyldimethoxysilane, tert-butylisopropyldimethoxysilane, cyclohexyl- methyldimethoxysilane, dicyclohexyldimethoxysilane, cyclohexyl-tert-butyldimethoxysilane, cyclopentylmethyldimethoxysilane, cyclopentylethyldimethoxysilane, dicyclopentyldimethoxysilane, cyclopentylcyclohexyldimethoxysilane, di(2-methylcyclopentyl)dimethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, phenyltriethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, propyltrimethoxysilane, propyltriethoxysilane, isopropyltrimethoxysilane, isopropyltriethoxysilane, butyltrimethoxysilane, butyltriethoxysilane,

isobutyltrimethoxysilane, isobutyltriethoxysilane, pentyltrimethoxysilane, isopentyltrimethoxysilane, cyclopentyltrimethoxysilane, cyclohexyltrimethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, n-propyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, etc. These organosilicon compounds can be used alone or in combination of two or more thereof. More preferably, the compound as external electron donor comprises at least one of dicyclopentyldimethoxysilane, diisopropyldimethoxysilane, diisobutyl- dimethoxysilane, cyclohexylmethyldimethoxysilane, diphenyldimethoxysilane, methyltert-butyldimethoxysilane, tetraethoxysilane, propyltriethoxysilane, isobutyltriethoxysilane.

The used amount of the alkyl aluminum compound can be a conventional amount in the art. Generally, the molar ratio of the aluminum in the alkyl aluminum compound to the titanium in the catalyst solid component is 20 to 500 : 1, preferably 50 to 500 : 1, more preferably 25 to 100 : 1.

In the propylene polymerization catalyst according to the present invention, the used amount of the external electron donor is not particularly limited. In a preferred embodiment, the molar ratio of the aluminum in the alkyl aluminum compound to the silicon in the external electron donor is 0.1 to 500 : 1, preferably 1 to 200 : 1, more preferably 3 to 100 : 1.

By increasing the polymerization temperature in the step (2) for preparing polypropylene, the process according to the present invention results in a polypropylene with narrow molecular weight distribution and good H regulation sensitivity, which can be used for producing products with high isotacticity and higher fluidity. With the addition of external electron donor, the preparation process results in the obtained polymer product having a significantly reduced xylene-soluble fraction. At the

same time, the process of the present invention further preferably uses a specific type of catalyst, which still has a relatively high polymerization activity when used at higher polymerization temperature after pre-polymerization. Hence, the process according to the present invention is of better promise for spreading and application in industrial implementation.

The narrow molecular-weight-distribution polypropylene of the present invention can be used in spinning, thin-wall injecting, and casting processes, and in preparation of transparent materials, etc.

Examples

The present invention is further illustrated in conjunction with the following examples. The protection scope of the present invention is not restricted by these examples, but is given in the appended claims.

The parameters or data in the present disclosure, including examples, were determined according to the following measuring methods.

1. Molecular weight distribution width index Mw/Mn: the molecular weight distribution of samples was measured by using PL-GPC 220 gel permeation chromatograph (Polymer Laboratories Company, Britain) combined with an IR5 infrared detector. Three Plgel 10μm MIXED-B columns were used in series and the column temperature was 150°C; 1,2,4-trichlorobenzene (containing 0.3g/1000mL antioxidant 2,6-di-tert-butyl-p-cresol) was used as the solvent and the mobile phase, the flow rate was 1.0 mL/min. A universal calibration was performed by using narrow distribution polystyrene standards, EasiCal PS-1, of PL Company.

2. Polydispersity index of high-molecular-weight tail in molecular weight distribution width, PI_{HT}: the peak molecular weight Mp, the weight-average molecular weight Mw and the Z-average molecular weight Mz were measured according to the

above method 1, wherein the unit was g/mol, and Formula (1) was used for calculation:

$$PI_{HT}=10^5* (Mz/Mp)/Mw \qquad (1)$$

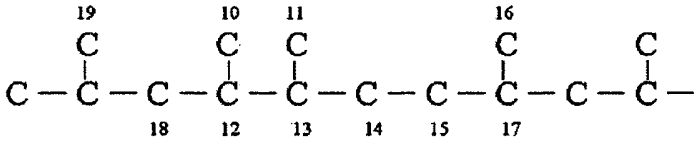
3. Measurement of pentad [mmmm] content: because in ^{13}C-NMR spectra, the methyl carbon zone with chemical shift of 19.5 to 22.5 ppm can provide tacticity information with relatively high resolution, the measurement results of this zone were used for calculating [mmmm] isotacticity, see equation (2):

$$[mmmm]\% = 100 * \frac{[mmmm]}{[mm]+[mr]+[rr]} \qquad (2)$$

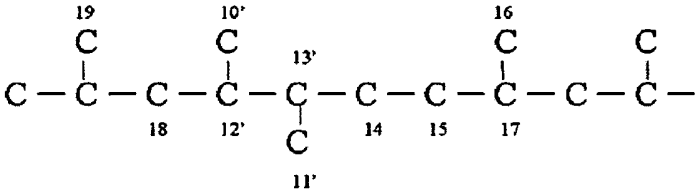
in which [mm], [mr], [rr] represent triad isotactic, isotactic-syndiotactic, syndiotactic-syndiotactic contents, respectively, and can be easily calculated from the spectra.

Measurement was performed by using a 400 MHz nuclear magnetic resonance spectrometer (NMR), Mode AVANCE III, of Bruker Company, Switzerland. Solvent is deuterated o-dichlorobenzene, 250mg sample/2.5mL solvent. In order to avoid oxidative degradation of samples during dissolution and data collection, 2 mg of BHT (2,6-di-t-butyl-4-methylphenol) antioxidant was added to samples. Samples were dissolved at 140°C, ^{13}C-NMR collection was performed at the test temperature of 125°C, with the detection head having a specification of 10 mm, with 90° pulse, with sampling time AQ of 5 seconds, with delay time D1 of 1 second, and with the times of scan of 6000 times. More details for identification of spectral peaks and the like could find in the references: (1) Hansen E W, Redford K. Nuclear Magnetic Resonance Spectroscopy of Polypropylene Homopolymers. In: Karger-Kocsis J, ed. Polypropylene: A-Z Reference. Dordrecht: Kluwer Publishers, 1999: 540-544; (2) Zambelli A, Macromolecules Vol. 8, No. 5, 1975: 687-688.

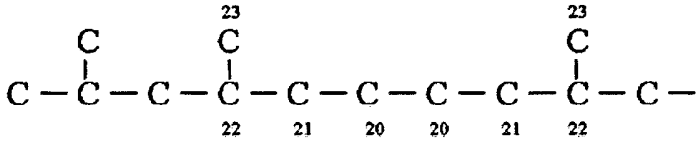
4. Detection of regio-irregularity caused by 2,1-insertion and 1,3-insertion of propylene: in the presence of some catalysts, the occurrence of "2,1" insertion and/or "1,3" insertion of the monomers during polymerization of propylene monomers results in destruction of tacticity of molecular chain structure, and the defect structures caused thereby are called herein collectively as "regio-irregularity", and regional defect structures of isotactic polypropylene have following structural schemes:



(a) head-head structure (erythro) caused by "2,1" insertion



(b) head-head structure (threo) caused by "2,1" insertion



(c) defect caused by "1,3" insertion

By ^{13}C-NMR analysis, occurrence frequency of "2,1" insertion and "1,3" insertion could be further calculated, that is:

$$\text{"2,1" insertion (\%)} = \frac{0.5I_{\alpha\beta}}{I_{\alpha\alpha}+I_{\alpha\beta}+I_{\alpha\delta}}$$

$$\text{"1,3" insertion (\%)} = \frac{0.5I_{\alpha\delta}}{I_{\alpha\alpha}+I_{\alpha\beta}+I_{\alpha\delta}}$$

The test conditions of ^{13}C-NMR were the same as those of method 3, while more details such as identification of spectral peaks and data processing could find in the references: (1) Grassi A, Zambelli A. Macromolecules, 1988, 21: 617-622; (2) Tsutsui T, Ishimaru N, Mizuno A, et al. Polymer, 1989, 30: 1350-1356.

5. Measurement of TREF (Temperature Rising Elution Fractionation) soluble fraction SF: TREF-300 Analyzer of Poly CHAR Company was used for the measurement, and specific process was as follows: 80 mg of a sample was weighed and dissolved in 40 mL of TCB (trichlorobenzene) solvent with 0.3% BHT at 150°C for 60 min, so that the sample was sufficiently dissolved to form a homogenous solution; 20 mL of the solution was fed to the columns, cooled at a rate of 0.2°C/min to 35°C, so that the sample gradually crystallized, isolated and precipitated on the columns during the decreasing of temperature according to crystallization capacity; it was kept at 35°C for 10 min and then the temperature was increased at a rate of 1.0°C/min to 140°C and elution was performed. During the elution, the flow rate in a solvent pump was controlled at 0.5 mL/min, the dissolved sample was continuously eluted by a solvent, and the correlation of the elution of the sample and the temperature was recorded. The percentage content of the eluate at 35°C was recorded as soluble fraction SF.

6. Measurement of crystallization temperature Tc: DIAMOND Mode DSC of PE Company was used, the instrument was calibrated with metal indium and zinc standards, the sample weight was about 5 mg, the atmosphere was nitrogen gas, the gas flow was 20 mL/min. Particular antioxidant-containing sample to be tested was heated at a rate of 10°C/min to 210°C, kept constant for 5 min to eliminate thermal history, then cooled at a rate of 10°C/min to 50°C, the crystallization exotherm curve was recorded, and the

temperature corresponding to the peak of the crystallization exotherm curve was recorded as crystallization temperature Tc.

7. Measurement of xylene-soluble fraction: the measurement was performed according to ASTM D5492-98.

8. Melt flow rate MFR: it was measured according to ISO 1133 at 230°C, 2.16 kg load.

9. Contents of titanium atom in the catalyst solid component and propylene polymerization catalyst component were measured by using the spectrophotometer 721 from Anhemeng (Tianjin) Sci & Tech Development Co., Ltd.

10. Particle size and particle size distribution of the alkoxy magnesium and the catalyst were measured by using Malvern Mastersizer TM 2000 laser diffraction method, and n-hexane was used as the dispersant (herein, SPAN=(D90-D10)/D50).

11. Measurement of m value of the carrier: 0.1 g of the carrier was taken, added with 10 mL of 1.2 mol/l aqueous hydrochloric acid, decomposed by shaking for 24 h, the contents of ethanol and 2-ethylhexanol therein were quantified by using gas chromatography, and then m value was calculated according to the following formula:

$$m = \frac{2\ (w1 \times 46.07)}{w2 \times 130.23 + w1 \times 46.07}$$

in which w1 was mass of 2-ethylhexanol, and w2 was mass of ethanol.

12. The content of internal electron donor in propylene polymerization catalyst component was measured by using Waters 600E liquid chromatograph or gas chromatograph.

Example 1:

1) Starting materials:

Preparation of main catalyst: a 16 L pressure-resistant reactor with a stirrer was sufficiently replaced with nitrogen

gas, and was added with 10 L of ethanol, 300 mL of 2-ethylhexanol, 11.2g of iodine, 8 g of magnesium chloride and 640 g of magnesium powder. Under stirring, the temperature of the system was elevated to 75°C for the reaction under reflux, until no more hydrogen gas was released. The reaction was terminated, 3 L of ethanol was used for washing, and after filtration and drying, sphere-like particulate dialkoxy magnesium carrier was obtained. The dialkoxy magnesium carrier had D50=30.2 μm, Span value of 0.81, m value of 0.015. 650g of the above dialkoxy magnesium carrier and 3250 mL of toluene and 65 mL of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane were formulated into a suspension. In a 16 L pressure-resistant reactor that was repeatedly replaced with highly pure nitrogen gas, 2600 mL of toluene and 3900 mL of titanium tetrachloride were added, heated to 80°C, then the formulated suspension was added to the reactor, kept constant at the temperature for 1 h, 65 mL of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane was added, slowly heated to 110°C, kept at the temperature constant for further 2 h, and press-filtrated to a solid. The obtained solid was added to a mixture liquid of 5070 mL of toluene and 3380 mL of titanium tetrachloride and treated under stirring at 110°C for 1 h, and such treatment was repeated for 3 times. After press filtration, the obtained solid was washed with hexane for 4 times, 600 mL per time, press-filtered, dried, to obtain the main catalyst solid component. The obtained catalyst solid component has a content of titanium atom of 4.1 wt%, and a content of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane of 11.9%.

Triethyl aluminum was used as the co-catalyst: propylene and hydrogen gas in polymerization grade were subjected to dewatering and deoxygenating before use, and hexane was subjected to dewatering before use.

2) Experimental device

The device employed a polymerization process of continuous pre-polymerization reactor+ horizontal gas phase reactor in series. The pre-polymerization reactor had a volume of 5L, was a vertical agitated vessel with jacketed cooling, the used stirring blades were turbine type inclined paddles, and the agitation rate was 500 rpm; the horizontal gas phase reactor had a volume of 0.2 m^3, and was a horizontal agitated vessel, the used stirring blades were T-type inclined paddles, the angle of inclination was 10°, the agitation rate was 100 rpm.

3) Experimental conditions:

Pre-polymerization of step (1): the reaction pressure was 2.5 MPa, the reaction temperature was 10°C, the reaction resident time was 12 minutes; the main catalyst, triethyl aluminum were fed at rates of 0.4 g/h, 0.058 mol/h, respectively; propylene was fed at rate of 10 kg/h. Pre-polymerization times is 65.

Gas phase polymerization of step (2): the reaction temperature was 98°C, the reaction pressure was 2.3MPa, the reaction resident time was 60 minutes; propylene was fed at rate of 30 kg/h; hydrogen gas was fed at rate of 0.24 g/h; and the molar ratio of hydrogen gas/propylene in reaction gas phase was 0.005.

4) Experimental results

The experiment was continuously performed for 48 h according to the above conditions, the operation of device was stable, the polymer obtained in the reaction was analyzed and measured and the results were shown in Table 1.

Example 2:

1) Starting materials (the same as those of Example 1)

2) Experimental device (the same as that of Example 1)

3) Experimental conditions

Pre-polymerization of step (1): the reaction pressure was 2.5 MPa, the reaction temperature was 10°C, the reaction time was 12 minutes; the main catalyst, triethyl aluminum were fed at rates of 0.4g/h, 0.058 mol/h, respectively; propylene was fed at rate of 10 kg/h. Pre-polymerization times is 65.

Gas phase polymerization of step (2): the reaction temperature was 91°C, the reaction pressure was 2.3MPa, the reaction time was 60 minutes; propylene was fed at rate of 30 kg/h; hydrogen gas was fed at rate of 0.4 g/h; and the molar ratio of hydrogen gas/propylene in reaction gas phase was 0.008.

4) Experimental results

The experiment was continuously performed for 48 h according to the above conditions, the operation of device was stable, the polymer obtained in the reaction was analyzed and measured and the results were shown in Table 1.

Example 3:

1) Starting materials (the same as those of Example 1)

2) Experimental device (the same as that of Example 1)

3) Experimental conditions

Pre-polymerization of step (1): the reaction pressure was 2.5 MPa, the reaction temperature was 10°C, the reaction time was 12 minutes; the main catalyst, triethyl aluminum, dicyclopentyldimethoxysilane DCPDMS (so-called "D-Donor") were fed at rates of 1.1g/h, 0.051 mol/h, 0.0082 mol/h, respectively; Al/Si(mol/mol)=6.2; propylene was fed at a rate of 10 kg/h. Pre-polymerization times is 90.

Gas phase polymerization of step (2): the reaction temperature was 98°C, the reaction pressure was 2.3MPa, the reaction time was 60 minutes; propylene was fed at a rate of 30

kg/h; hydrogen gas was fed at a rate of 0.6 g/h; and the molar ratio of hydrogen gas/propylene in the reaction gas phase was 0.012.

4) Experimental results

The experiment was continuously performed for 48 h according to the above conditions, the operation of device was stable, the polymer obtained in the reaction was analyzed and measured and the results were shown in Table 1.

Example 4:

1) Starting materials (the same as those of Example 1)

2) Experimental device (the same as that of Example 1)

3) Experimental conditions

Pre-polymerization of step (1): the reaction pressure was 2.5 MPa, the reaction temperature was 10°C, the reaction time was 12 minutes; the main catalyst, triethyl aluminum, diisobutyldimethoxysilane (DIBDMS, so-called "B-Donor") were fed at rates of 1.0g/h, 0.054 mol/h, 0.0087 mol/h, respectively; Al/Si(mol/mol)=6.2; propylene was fed at a rate of 10 kg/h. Pre-polymerization times is 80.

Gas phase polymerization of step (2): the reaction temperature was 91°C, the reaction pressure was 2.3MPa, the reaction time was 60 minutes; propylene was fed at a rate of 30 kg/h; hydrogen gas was fed at a rate of 0.75 g/h; and the molar ratio of hydrogen gas/propylene in the reaction gas phase was 0.015.

4) Experimental results

The experiment was continuously performed for 48 h according to the above conditions, the operation of device was stable, the polymer obtained in the reaction was analyzed and measured and the results were shown in Table 1.

Comparative Example 1:

1) Starting materials (the same as those of Example 1)

2) Experimental device (the same as that of Example 1)

3) Experimental conditions

Pre-polymerization of step (1): the reaction pressure was 2.5 MPa, the reaction temperature was 10°C, the reaction time was 12 minutes; the main catalyst, triethyl aluminum were fed at rates of 0.4g/h, 0.058 mol/h, respectively; propylene was fed at a rate of 10 kg/h. Pre-polymerization times is 65.

Gas phase polymerization of step (2): the reaction temperature was 66°C, the reaction pressure was 2.3MPa, the reaction time was 60 minutes; propylene was fed at a rate of 30 kg/h; hydrogen gas was fed at a rate of 1.25 g/h; and the molar ratio of hydrogen gas/propylene in the reaction gas phase was 0.025.

4) Experimental results

The experiment was continuously performed for 48 h according to the above conditions, the operation of the device was stable, the polymer obtained in the reaction was analyzed and measured and the results were shown in Table 1.

Comparative Example 2:

1) Starting materials (the same as those of Example 1)

2) Experimental device (the same as that of Example 1)

3) Experimental conditions

Pre-polymerization of step (1): the reaction pressure was 2.5 MPa, the reaction temperature was 10°C, the reaction time was 12 minutes; the main catalyst, triethyl aluminum, dicyclopentyldimethoxysilane DCPDMS (so-called "D-Donor") were fed at rates of 1.1g/h, 0.051 mol/h, 0.0082 mol/h, respectively;

Al/Si(mol/mol)=6.2; propylene was fed at a rate of 10 kg/h. Pre-polymerization times is 90.

Gas phase polymerization of step (2): the reaction temperature was 66°C, the reaction pressure was 2.3MPa, the reaction time was 60 minutes; propylene was fed at a rate of 30 kg/h; hydrogen gas was fed at a rate of 2.5 g/h; and the molar ratio of hydrogen gas/propylene in the reaction gas phase was 0.05.

4) Experimental results

The experiment was continuously performed for 48 h according to the above conditions, the operation of the device was stable, the polymer obtained in the reaction was analyzed and measured and the results were shown in Table 1.

Comparative Example 3:

1) Starting materials (the same as those of Example 1)

2) Experimental device (the same as that of Example 1)

3) Experimental conditions

Without pre-polymerization, the catalyst was directly added to the gas phase reactor. Main catalyst, triethyl aluminum were fed at rates of 0.4g/h, 0.058 mol/h, respectively; the gas phase polymerization temperature was 98°C, the reaction pressure was 2.3MPa, the reaction time was 60 minutes; propylene was fed at a rate of 30 kg/h; hydrogen gas was fed at a rate of 0.24 g/h; and the molar ratio of hydrogen gas/propylene in the reaction gas phase was 0.005.

4) Experimental results

The experiment was performed according to the above conditions, and showed too low polymerization activity, and the results were shown in Table 1.

Comparative Example 4:

Commercially available polypropylene product with high fluidity, narrow molecular weight distribution, with the brand of H30S, was prepared by degradation using peroxide by Zhenhai Oil Refining and Chemical Company.

Table 1: Polymerization conditions and properties of polymers

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
External electron donor	None	None	D-Donor	B-Donor	None	D-Donor	None	--
Pre-polymerization temperature, °C	10	10	10	10	10	10	Without pre-polymerization	--
Pre-polymerization time, min	12	12	12	12	12	12	-	--
Polymerization temperature, °C	98	91	98	91	66	66	98	--
H_2/propylene ratio in gas phase reactor (mol/mol)	0.005	0.008	0.012	0.015	0.025	0.05	0.005	--
Activity, KgPP/gCat.h	33	45	28	35	50	40	3.0	--
Mw, 10^4g/mol	17.9	17.8	18.3	17.5	17.6	18.1	-	18.7
Mw/Mn	3.8	4.4	4.3	4.2	5.6	7.0	-	4.3
PI_{HT}	2.35	2.33	2.3	2.41	2.96	3.1	-	1.72
[mmmm]%	89.2	90.1	92.9	94.4	89.8	92.6	-	91.9
2,1 insertion and/or 1,3 insertion of propylene	0	0	0	0	0	0	-	0
SF (analytic type TREF), %	3.95	3.05	1.85	1.60	4.10	2.7	-	2.35
Xylene-soluble fraction, wt%	4.09	3.23	2.06	1.52	4.43	3.2	-	2.37
MFR, g/10min	46.8	47.6	44.9	51.7	52.2	50.5	-	40.0
Tc, °C	116.2	117.2	116.8	116.4	118.0	118.6	-	112.8

It can be seen from the data of Table 1:

1. The narrow molecular-weight-distribution polypropylene as prepared according to the present invention has relatively high isotacticity, and polypropylenes with different isotacticities can be obtained by regulating reaction conditions according to requirements, and they are free of regio-irregularity caused by 2,1-insertion and 1,3-insertion and the like of propylene.

2. By comparing the narrow molecular-weight-distribution polypropylene of the present invention with that of Comparative Example 4, the molecular weight distribution width expressed as the ratio of weight-average molecular weight to number-average molecular weight can reach and even exceed the level of narrow molecular weight distribution of degradation process. At the same time, the product of the present invention is obtained according to direct polymerization, and does not need degradation, and thus achieves low cost, environmental protection and energy saving; the polydispersity index of high-molecular-weight tail in molecular weight distribution width, PI_{HT}, is significantly different from that of degradation process, so that the crystallization temperature of polypropylene of the present invention is obviously higher than that of the narrow molecular-weight-distribution polypropylene of degradation process, which indicates that it has shorter molding cycle in comparison with the degradation process and can effectively increase molding efficiency.

3. The results of Comparative Example 1 show that: the polymer product obtained by conventional polymerization at 66°C has a wide molecular weight distribution. In comparison with Comparative Example 1, the process for preparing the narrow molecular-weight-distribution polypropylene (Example 1 and Example 2) of the present invention results in the polymer product having narrower molecular weight distribution, and good

H-regulation sensitivity, and the obtained polymerized products have lower xylene-soluble fractions.

4. In comparison with the polymer obtained without addition of external electron donors, the polymers obtained with addition of external electron donor (Example 3 and Example 4) have significantly increased isotacticity, and significantly decreased xylene-soluble fraction. In comparison with Comparative Example 2, the polypropylenes according to the present invention of Example 3 and Example 4 have narrower molecular weight distribution, and better H-regulation sensitivity, and the obtained polymerized products have lower xylene-soluble fractions.

5. The results of Comparative Example 3 show that without pre-polymerization step, direct polymerization at a relatively high temperature of 98°C exhibits a polymerization activity of only 3000 times and no commercial application value.

Clauses:

1. A polypropylene, characterized in that the polypropylene has a molecular weight distribution index Mw/Mn of from 2.5 to 5.5, preferably from 3.0 to 4.9; and a polydispersity index of high-molecular-weight tail in molecular weight distribution width, PI_{HT}, of greater than 1.9, preferably greater than 2.1.

2. The polypropylene according to claim 1, characterized in that the polypropylene has isotactic pentad [mmmm] sequences in a content of greater than 85%, preferably greater than 90%, more preferably greater than 93%.

3. The polypropylene according to claim 1 or 2, characterized in that the polypropylene is free of regio-irregularity caused by 2,1-insertion and 1,3-insertion of propylene.

4. The polypropylene according to any one of claims 1 to 3, characterized in that the polypropylene has a crystallization temperature, Tc, of higher than 113°C, preferably higher than 115°C.

5. The polypropylene according to any one of claims 1 to 4, characterized in that the polypropylene has a xylene-soluble fraction of less than 4.4 wt%, preferably less than 2.3 wt%, more preferably less than 1.6 wt%.

6. The polypropylene according to any one of claims 1 to 5, characterized in that the polypropylene has a melt flow rate, MFR, of 0.01 to 1000 g/10min, preferably 1 to 1000 g/10min, more preferably 1 to 399 g/10min.

7. The polypropylene according to any one of claims 1 to 6, characterized in that the polypropylene is directly prepared by polymerization in a reactor.

8. The polypropylene according to claim 7, characterized in that the polypropylene is prepared by a process comprising the following steps:

(1) pre-polymerizing propylene in the presence of a Ziegler-Natta catalyst,

(2) polymerizing propylene in the presence of a prepolymer of propylene obtained in step (1), in a gas phase, at the polymerization temperature of from 91 to 150°C, preferably from 91 to 110°C.

9. The polypropylene according to claim 8, characterized in that the Ziegler-Natta catalyst comprises a reaction product of the following components:

(1) a titanium-containing solid catalyst component, which is a reaction product of contacting an alkoxy magnesium compound, a titanium compound and an internal electron donor compound;

wherein the titanium compound is selected from at least one compound of Formula (I):

$$Ti(OR)_{4-n}X_n \qquad (I)$$

in which

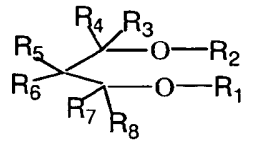
R is selected from C_1-C_{14} aliphatic hydrocarbonyl or aromatic hydrocarbonyl;

X is halogen;

n is an integer selected from 0 to 4;

when n is equal to or less than 2, the R groups present are the same or different;

the internal electron donor compound is selected from at least one diether compound of Formula (IV),



(IV)

in which

R_1 and R_2 are the same or different, and each independently selected from C_1-C_{20} linear, branched and cyclic aliphatic groups;

R_3, R_4, R_5, R_6, R_7 and R_8 are the same or different, and each independently selected from hydrogen, halogen atom and linear or branched C_1- C_{20} alkyl, C_3- C_{20} cycloalkyl, C_6- C_{20} aryl, C_7- C_{20} alkylaryl and C_7- C_{20} arylalkyl, optionally, R_3 to R_8 can be bonded to each other to form a ring;

preferably, R_1 and R_2 are the same or different, and each independently selected from C_1-C_6 linear or branched alkyl;

R_5 and R_6 are the same or different, and each independently selected from linear or branched C_1-C_{10} alkyl, or C_3-C_{10} cycloalkyl;

(2) an alkyl aluminum compound;

preferably, further comprising (3) an external electron donor compound.

10. The polypropylene according to claim 9, characterized in that the alkoxy magnesium compound is selected from at least one compound of the formula $Mg(OR^1)_{2-m}(OR^2)_m$, wherein R^1 and R^2 are the same or different, and each are selected from one of C_1-C_8 linear or branched alkyl groups, and $0 \leq m \leq 2$.

11. The polypropylene according to claim 10, characterized in that the alkoxy magnesium compound is prepared by reaction of magnesium metal, the alcohol R^1OH, R^2OH corresponding to the

alkoxy groups and a mixed halogenating agent in an atmosphere of inert gas, wherein the molar ratio of magnesium metal to halogen atom in the mixed halogenating agent is 1:0.0002 to 1:0.2, the weight ratio of the alcohol to magnesium is 4:1 to 50:1, wherein the molar ratio x of R^1OH to R^2OH is $3(2-m)/m>x>(2-m)/m$, and the mixed halogenating agent is a combination of halogen and halogen compound.

12. The polypropylene according to any one of claims 9 to 11, characterized in that the external electron donor compound is an organosilicon compound of Formula (VII),

$$R^{1''}_{m''}R^{2''}_{n''}Si(OR^{3''})_{4-m''-n''} \qquad \textbf{(VII)}$$

in which

$R^{1''}$ and $R^{2''}$ are the same or different, each are one of halogen, hydrogen atom, alkyl with 1 to 20 carbon atoms, cycloalkyl with 3 to 20 carbon atoms, aryl with 6 to 20 carbon atoms and halogenated alkyl with 1 to 20 carbon atoms;

$R^{3''}$ is one of alkyl with 1 to 20 carbon atoms, cycloalkyl with 3 to 20 carbon atoms, aryl with 6 to 20 carbon atoms and halogenated alkyl with 1 to 20 carbon atoms;

m'' and n'' each are an integer of 0 to 3, and $m''+n''<4$.

13. A process for preparing the polypropylene according to any one of claims 1 to 6, comprising the following steps:

(1) pre-polymerizing propylene in the presence of a Ziegler-Natta catalyst,

(2) polymerizing propylene in the presence of a prepolymer of propylene obtained in step (1), in a gas phase, at the polymerization temperature of from 91 to 150°C, preferably from 91 to 110°C.

14. The process according to claim 13, characterized in that the process comprises the following steps:

(1) pre-polymerizing propylene in the presence of a Ziegler-Natta catalyst, in a gas phase or a liquid phase, at -10°C to 50°C, and 0.1 to 10.0 MPa to obtain a prepolymer of propylene, wherein pre-polymerization times is controlled as 2 to 3000 g polymer/g catalyst, preferably 3 to 2000 g polymer/g catalyst;

(2) homopolymerizing propylene in the presence of the prepolymer of propylene obtained in step (1), in a gas phase, at 91 to 150°C, preferably 91 to 110°C, and 1.0 to 6.0 MPa, for the polymerization time of 0.5 to 4.0 h, to obtain the propylene polymer.

15. The process according to claim 14, characterized in that the step (1) and step (2) are performed discontinuously in the same one reactor, or continuously in different reactors.

16. The process according to any one of claims 13 to 15, characterized in that in the step (1), the pre-polymerization temperature of propylene is controlled at 0 to 30°C, preferably 10 to 25°C; the pre-polymerization pressure is 1.0 to 6.0 MPa, preferably 1.5 to 5.5 MPa.

17. The process according to any one of claims 13 to 16, characterized in that the step (1) is liquid phase bulk pre-polymerization of propylene at a temperature of 0 to 30°C; and the step (2) is gas phase homopolymerization of propylene at a temperature of 91 to 110°C.

18. The process according to any one of claims 13 to 17, characterized in that the gas phase polymerization of propylene in the step (2) is performed in a horizontal reactor which has

a horizontal mixer shaft, a stirring speed of 10 to 150 rpm, and the mixing blades whose types are selected from T type, rectangle, inclined paddle, door type, wedge-shaped or any combination thereof, and which uses a quenching liquid to remove heat.

19. The process according to any one of claims 13 to 18, characterized in that the Ziegler-Natta catalyst comprises a reaction product of the following components:

(1) a titanium-containing solid catalyst component;

(2) an alkyl aluminum compound;

preferably, further comprising (3) an external electron donor compound.

20. The process according to claim 19, characterized in that the titanium-containing solid catalyst component as the component (1) is a reaction product of contacting an alkoxy magnesium compound, a titanium compound and an internal electron donor compound;

wherein the titanium compound is selected from at least one compound of Formula (I):

$$Ti(OR)_{4-n}X_n \qquad (I)$$

in which

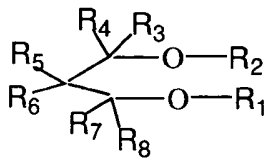
R is selected from C_1-C_{14} aliphatic hydrocarbonyl or aromatic hydrocarbonyl;

X is halogen;

n is an integer selected from 0 to 4;

when n is equal to or less than 2, the R groups present are the same or different;

the internal electron donor compound is selected from at least one diether compound of Formula (IV),



(IV)

in which

R_1 and R_2 are the same or different, and each independently selected from C_1-C_{20} linear, branched and cyclic aliphatic groups;

R_3, R_4, R_5, R_6, R_7 and R_8 are the same or different, and each independently selected from hydrogen, halogen atom and linear or branched C_1- C_{20} alkyl, C_3- C_{20} cycloalkyl, C_6- C_{20} aryl, C_7- C_{20} alkylaryl and C_7- C_{20} arylalkyl, optionally, R_3 to R_8 can be bonded to each other to form a ring;

preferably, R_1 and R_2 are the same or different, and each independently selected from C_1-C_6 linear or branched alkyl;

R_5 and R_6 are the same or different, and each independently selected from linear or branched C_1-C_{10} alkyl, or C_3-C_{10} cycloalkyl.

21. The process according to claim 20, characterized in that the alkoxy magnesium compound is selected from at least one compound of the formula $Mg(OR^1)_{2-m}(OR^2)_m$, wherein R^1 and R^2 are the same or different, and each are selected from one of C_1-C_8 linear or branched alkyl groups, and $0 \leq m \leq 2$.

22. The process according to claim 21, characterized in that in the formula, R^1 is ethyl, R^2 is (2-ethyl)hexyl, $0.001 \leq m \leq 0.5$, preferably $0.001 \leq m \leq 0.25$, more preferably $0.001 \leq m \leq 0.1$.

23. The process according to any one of claims 20 to 22, characterized in that the alkoxy magnesium compound has sphere-like appearance, an average particle size D50 of 10 to 150 μm, preferably 15 to 100 μm, more preferably 18 to 80 μm, and

a particle size distribution index SPAN<1.1, preferably a particle size distribution index SPAN<1.05, wherein SPAN is calculated by the following Formula (III):

$$\mathbf{SPAN=(D90-D10)/D50} \quad \mathbf{(III)}$$

in which

D90 represents a particle diameter corresponding to an accumulation weight fraction of 90%;

D10 represents a particle diameter corresponding to an accumulation weight fraction of 10%; and

D50 represents a particle diameter corresponding to an accumulation weight fraction of 50%.

24. The process according to claim 23, characterized in that the alkoxy magnesium compound is prepared by the following process: under the protection of an inert gas atmosphere, reacting an alcohol and magnesium metal as staring materials with a mixed halogenating agent to prepare sphere-like particulate dialkoxy magnesium; wherein the weight ratio of the alcohol to magnesium is 4 to 50 : 1; the alcohol is a linear or branched monoalcohol or polyalcohol; the halogenating agent is selected from at least one of elementary halogens and halides, and is used with the molar ratio of halogen atom to magnesium of 0.0002 to 0.2 : 1.

25. The process according to any one of claims 19 to 24, characterized in that the external electron donor compound is an organosilicon compound of Formula (VII),

$$\mathbf{R^{1''}_{m''}R^{2''}_{n''}Si(OR^{3''})_{4-m''-n''}} \quad \mathbf{(VII)}$$

in which

$R^{1''}$ and $R^{2''}$ are the same or different, and each are one of halogen, hydrogen atom, alkyl with 1 to 20 carbon atoms, cycloalkyl with 3 to 20 carbon atoms, aryl with 6 to 20 carbon atoms and halogenated alkyl with 1 to 20 carbon atoms;

$R^{3''}$ is one of alkyl with 1 to 20 carbon atoms, cycloalkyl with 3 to 20 carbon atoms, aryl with 6 to 20 carbon atoms and halogenated alkyl with 1 to 20 carbon atoms;

m'' and n'' each are an integer of 0 to 3, and $m'' + n'' < 4$.

26. Use of the polypropylene according to any one of claims 1 to 12 or the polypropylene as prepared by the process according to any one of claims 13 to 25 in spinning, thin-wall injecting, or casting processes, or in the preparation of transparent materials.

CONCLUSIES

1. Een polypropyleen, met het kenmerk dat de polypropyleen een molecuulgewicht distributie-index Mw/Mn bezit van vanaf 2,5 tot en met 5,5, de voorkeur geniet vanaf 3,0 tot en met 4,9; en een polydispersiteitsindex van een hoog molecuulgewichtsstaart met een moleculair gewicht distributiebreedte, PI_{HT}, van meer dan 1,9, de voorkeur geniet meer dan 2,1.

2. De polypropyleen volgens conclusie 1, met het kenmerk dat de polypropyleen iso-tactische pentad [mmmm] sequenties bezit in een hoeveelheid van meer dan 85%, de voorkeur geniet meer dan 90%, meer de voorkeur geniet meer dan 93%.

3. De polypropyleen volgens conclusie 1 of 2, met het kenmerk dat de polypropyleen vrij is van regio-irregulariteit veroorzaakt door 2,1-insertie en 1,3-insertie van propyleen.

4. De polypropyleen volgens één van de conclusies 1 tot en met 3, met het kenmerk dat de polypropyleen een kristallisatietemperatuur, Tc, bezit van meer dan 113°C, de voorkeur geniet meer dan 115°C.

5. De polypropyleen volgens één van de conclusies 1 tot en met 4, met het kenmerk dat de polypropyleen een xyleenoplosbare fractie bezit van minder dan 4,4 gewichts%, de voorkeur geniet minder dan 2,3 gewichts%, meer voorkeur geniet minder dan 1,6 gewichts%.

6. De polypropyleen volgens één van de conclusies 1 tot en met 5, met het kenmerk dat de polypropyleen een smeltstroomsnelheid, MFR, bezit van 0,01 tot en met

1000 g/10min, de voorkeur geniet 1 tot en met 1000 g/10min, meer voorkeur geniet 1 tot en met 399 g/10min.

7. De polypropyleen volgens één van de conclusies 1 tot en met 6, met het kenmerk dat de polypropyleen direct wordt bereid door middel van polymerisatie in een reactor.

8. De polypropyleen volgens conclusie 7, met het kenmerk dat de polypropyleen wordt bereid door gebruik te maken van een werkwijze omvattende de volgende stappen:

(1) het pre-polymeriseren van propyleen in de aanwezigheid van een Ziegler-Natta katalysator,

(2) het polymeriseren van propyleen in de aanwezigheid van een prepolymeer van de propyleen verkregen in stap (1), in een gasfase, bij een polymerisatietemperatuur vanaf 91 tot en met 150°C, de voorkeur geniet vanaf 91 tot en met 110°C.

9. De polypropyleen volgens conclusie 8, met het kenmerk dat de Ziegler-Natta katalysator een reactieproduct omvat van de volgende componenten:

(1) een titaniumbevattende vaste katalysatorcomponent, welke een reactieproduct is van het in contact brengen van een alkoxy magnesiumverbinding, een titaniumverbinding en een interne elektron donorverbinding; waarbij de titanium verbinding wordt geselecteerd uit ten minste één verbinding volgens Formule (I):

$$\mathbf{Ti(OR)_{4-n}X_n} \qquad \mathbf{(I)}$$

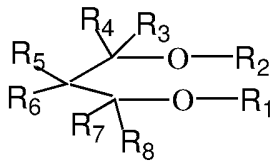
waarin

R wordt geselecteerd uit een C_1 tot en met c_{14} alifatische waterstofcarbonyl of een aromatische waterstofcarbonyl;

X is een halogeen;

n is een geheel getal geselecteerd uit 0 tot en met 4; waarbij indien n gelijk is of minder dan 2, de aanwezige R groepen hetzelfde kunnen zijn of verschillend;

de interne elektron donorverbinding wordt geselecteerd uit ten minste één di-etherverbinding volgens Formule (IV),



(IV)

waarbij

R_1 en R_2 hetzelfde of verschillend zijn en elk onafhankelijk wordt geselecteerd uit C_1 tot en met C_{20} lineaire, vertakte en cyclische alifatische groepen;

R_3, R_4, R_5, R_6, R_7 en R_8 zijn hetzelfde of verschillend en elk wordt onafhankelijk geselecteerd uit een waterstof, een halogeenatoom en een lineaire of vertakte C_1 tot en met C_{20} alkyl, een C_3 tot en met C_{20} cycloalkyl, een C_6 tot en met C_{20} aryl, een C_7 tot en met C_{20} alkylaryl en een C_7 tot en met C_{20} arylalkyl, optioneel kunnen R_3 tot en met R_8 met elkaar zijn verbonden zodat een ring gevormd wordt;

bij voorkeur zijn R_1 en R_2 hetzelfde of verschillend en elk zijn onafhankelijk geselecteerd uit C_1 tot en met C_6 lineaire of vertakte alkyl; R_5 en R_6 zijn hetzelfde of verschillend en elk onafhankelijk geselecteerd uit een lineaire of vertakte C_1 tot en met C_{10} alkyl, of een C_3 tot en met C_{10} cycloalkyl;

(2) een alkyl aluminiumverbinding;
bij voorkeur verder omvattende (3) een externe elektron donorverbinding.

10. De polypropyleen volgens conclusie 9, met het kenmerk dat de alkoxy magnesiumverbinding wordt geselecteerd uit ten minste één verbinding volgens de formule $Mg(OR^1)_{2-m}(OR^2)_m$, waarbij R^1 and R^2 hetzelfde zijn of verschillend, en elk wordt geselecteerd uit één van C_1 tot en met C_8 lineaire of vertakte alkyl groepen, $0 \leq m \leq 2$.

11. De polypropyleen volgens conclusie 10, met het kenmerk dat de alkoxy magnesiumverbinding wordt bereid door middel van een reactie van een magnesiummetaal, de alcohol R^1OH, R^2OH welke overeenkomt met alkoxy groepen en een gemengde halogenerende stof in een atmosfeer bestaande uit een inert gas, waarbij de molaire verhouding van het magnesiummetaal ten opzichte van het halogeenatoom in de gemengde halogenerende stof 1:0,0002 tot en met 1:0,2 is, de gewichtsverhouding van de alcohol ten opzichte van magnesium is 4:1 tot en met 50:1, waarbij de molaire verhouding x van R^1OH tot R^2OH $3(2-m)/m>x>(2-m)/m$ is, en de gemengde halogenerende stof is een combinatie van een halogeen en een halogeenverbinding.

12. De polypropyleen volgens één van de conclusies 1 tot en met 11, met het kenmerk dat de externe elektron donorverbinding een organosiliconverbinding is volgens de Formule (VII),

$$\mathbf{R^{1''}_{m''}R^{2''}_{n''}Si(OR^{3''})_{4-m''-n''}} \qquad \mathbf{(VII)}$$

waarbij

$R^{1''}$ en $R^{2''}$ hetzelfde zijn of verschillend en elk zijn één van een halogeen, een waterstofatoom, een alkyl met 1 tot en met 20 koolstofatomen, een cycloalkyl met 3 tot en met 20 koolstofatomen, een aryl met 6 tot en met 20 koolstofatomen en een gehalogeneerde alkyl met 1 tot en met 20 koolstofatomen;

$R^{3''}$ is één van een alkyl met 1 tot en met 20 koolstofatomen, een cycloalkyl met 3 tot en met 20 koolstofatomen, een aryl met 6 tot en met 20 koolstofatomen en een gehalogeneerde alkyl met 1 tot en met 20 koolstofatomen;

m'' en n'' zijn elk een geheel getal van 0 tot en met 3, en $m'' + n'' < 4$.

13. Een werkwijze voor het bereiden van de polypropyleen volgens één van de conclusies 1 tot en met 6, omvattende de volgende stappen:

(1) het prepolymeriseren van propyleen in de aanwezigheid van een Ziegler-Natta katalysator,

(2) het polymeriseren van propyleen in de aanwezigheid van een prepolymeer van propyleen verkregen in stap (1), in een gasfase, bij een polymerisatietemperatuur vanaf 91 tot en met 150°C, de voorkeur geniet vanaf 91 tot en met 110°C.

14. De werkwijze volgens conclusie 13, met het kenmerk dat de werkwijze de volgende stappen omvat:

(1) het prepolymeriseren van propyleen in aanwezigheid van een Ziegler-Natta katalysator, in een gasfase of een vloeistoffase, bij -10°C tot en met 50°C, en 0,1 tot en met 10,0 MPa voor het verkrijgen van een prepolymeer van propyleen, waarbij de prepolymerisatietijden worden

gecontroleerd voor het verkrijgen van 2 tot en met 3000 g polymeer/g katalysator, de voorkeur geniet 3 tot en met 2000 g polymeer/g katalysator;

(2) het homopolymeriseren van propyleen in de aanwezigheid van de prepolymeer van de propyleen verkregen in stap (1), in een gasfase, bij 91 tot en met 150°C, de voorkeur geniet 91 tot en met 110°C, en 1,0 tot en met 6,0 MPa gedurende een polymerisatietijd van 0,5 tot en met 4 uur voor het verkrijgen van de propyleen polymeer.

15. De werkwijze volgens conclusie 14, met het kenmerk dat de stap (1) en de stap (2) discontinu worden uitgevoerd in dezelfde één reactor, of continu in verschillende reactoren.

16. De werkwijze volgens één van de conclusies 13 tot en met 15, met het kenmerk dat in stap (1) de prepolymerisatietemperatuur van propyleen wordt gehouden op 0 tot en met 30°C, de voorkeur geniet 10 tot en met 25°C; de prepolymerisatiedruk is 1,0 tot en met 6,0 MPa, de voorkeur geniet 1,5 tot en met 5,5 MPa.

17. De werkwijze volgens één van de conclusies 13 tot en met 16, met het kenmerk dat stap (1) een vloeistoffase bulk prepolymerisatie van propyleen is bij een temperatuur van 0 tot en met 30°C; en stap (2) is een gasfase homopolymerisatie van propyleen bij een temperatuur van 91 tot en met 110°C.

18. De werkwijze volgens één van de conclusies 13 tot en met 17, met het kenmerk dat de gasfase polymerisatie van propyleen in stap (2) wordt uitgevoerd in een horizontale reactor welke een horizontale mengschaft bezit, een roersnelheid van 10 tot en met 150 rpm, en de mengbladen die typen zijn die

geselecteerd worden uit een T-type, een rechthoek, een schoep onder een hoek, een deurtype, een driehoektype of enige combinatie daarvan, en welke gebruik maakt van een quench vloeistof voor het verwijderen van de warmte.

19. De werkwijze volgens één van de conclusies 13 tot en met 18, met het kenmerk dat de Ziegler-Natta katalysator een reactieproduct omvat van de volgende componenten:

(1) een titaniumbevattende vaste katalysatorcomponent;

(2) een alkylaluminiumverbinding;

bij voorkeur verder omvattende (3) een externe elektron donoorverbinging.

20. De werkwijze volgens conclusie 19, met het kenmerk dat de titaniumbevattende vaste katalysatorcomponent als component (1) een reactieproduct is van het in contact brengen van een alkoxy magnesiumverbinding, een titaniumverbinding en een interne elektron donoorverbinding;

waarbij de titanium verbinding wordt geselecteerd uit ten minste één verbinding volgens de Formule (I):

$$\mathbf{Ti(OR)_{4-n}X_n} \qquad \mathbf{(I)}$$

waarin

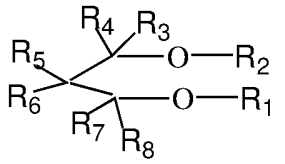
R wordt geselecteerd uit een C_1 tot en met C_{14} alifatische waterstofcarbonyl of een aromatische waterstofcarbonyl;

X is een halogeen;

n is een geheel getal geselecteerd uit 0 tot en met 4;

waarbij indien n gelijk is of minder dan 2, de aanwezige R groepen hetzelfde zijn of verschillend;

de interne elektron donoorverbinding wordt geselecteerd uit ten minste één di-etherverbinding volgens Formule (IV),



(IV)

waarbij

R_1 en R_2 hetzelfde of verschillend zijn en elk onafhankelijk wordt geselecteerd uit C_1 tot en met C_{20} lineaire, vertakte en cyclische alifatische groepen; R_3, R_4, R_5, R_6, R_7 en R_8 zijn hetzelfde of verschillend en elk onafhankelijk wordt geselecteerd uit een waterstof, een halogeenatoom en een lineaire of vertakte C_1 tot en met C_{20} alkyl, een C_3 tot en met C_{20} cycloalkyl, een C_6 tot en met C_{20} aryl, een C_7 tot en met C_{20} alkylaryl en een C_7 tot en met C_{20} arylalkyl, optioneel kunnen R_3 tot en met R_8 met elkaar zijn verbonden zodat een ring gevormd wordt;
bij voorkeur zijn R_1 en R_2 hetzelfde of verschillend en elk is onafhankelijk geselecteerd uit een C_1 tot en met C_6 lineaire of vertakte alkyl; R_5 en R_6 zijn hetzelfde of verschillend en elk onafhankelijk geselecteerd uit een lineaire of vertakte C_1 tot en met C_{10} alkyl, of een C_3 tot en met C_{10} cycloalkyl.

21. De werkwijze volgens conclusie 20, met het kenmerk dat de alkoxy magnesiumverbinding wordt geselecteerd uit ten minste één verbinding volgens de formule $Mg(OR^1)_{2-m}(OR^2)_m$, waarbij R^1 and R^2 hetzelfde zijn of verschillend, en elk wordt geselecteerd uit één van C_1 tot en met C_8 lineaire of vertakte alkyl groepen, en $0 \leq m \leq 2$.

22. De werkwijze volgens conclusie 21, met het kenmerk dat in de formule, R^1 ethyl is, R^2 is (2-ethyl)hexyl, $0,001 \leq m \leq 0,5$, de voorkeur geniet $0,001 \leq m \leq 0,25$, meer de voorkeur geniet $0,001 \leq m \leq 0,1$.

23. De werkwijze volgens één van de conclusies 20 tot en met 22, met het kenmerk dat de alkoxy magnesiumverbinding een op een sfeer gelijkend uiterlijk bezit, een gemiddelde deeltjesgrootte D50 van 10 tot en met 150 µm, de voorkeur geniet 15 tot en met 100 µm, meer de voorkeur geniet 18 tot en met 80 µm, en een deeltjesgrootte distributie-index SPAN<1,1, de voorkeur geniet een deeltjesgrootte distributie-index SPAN<1,05, waarbij SPAN wordt berekend volgens de Formule (III):

SPAN=(D90-D10)/D50 (III)

waarbij
D90 de deeltjesdiameter weergeeft welke overeenkomt met een accumulatiegewichtsfractie van 90%;
D10 geeft de deeltjesdiameter weer welke overeenkomt met een accumulatiegewichtsfractie van 10%; en
D50 geeft de deeltjesdiameter weer welke overeenkomt met een accumulatiegewichtsfractie van 50%.

24. De werkwijze volgens conclusie 23, met het kenmerk dat de alkoxy magnesiumverbinding wordt bereid door gebruik te maken van de volgende werkwijze: onder de bescherming van een inerte gasatmosfeer, het laten reageren van alcohol en een magnesiummetaal als uitgangsmaterialen met een gemengde halogenerende stof voor het bereiden van op een sfeer gelijkende deeltjes dialkoxy magnesium; waarbij de gewichtsverhouding van de alcohol ten opzichte van het magnesium 4:1 tot en met 50:1

is; de alcohol is een lineaire of vertakte monoalcohol of polyalcohol; de halogenerende stof wordt geselecteerd uit ten minste één van elementaire halogenen en haliden, en deze wordt gebruikt in een molaire verhouding van het halogeenatoom ten opzichte van het agnesium van 0,0002 tot en met 0,2:1.

25. De werkwijze volgens één van de conclusies 19 tot en met 24, met het kenmerk dat de externe elektron donoorverbinding een organosiliconverbinding is volgens de Formule (VII),

$$R^{1''}_{m''}R^{2''}_{n''}Si(OR^{3''})_{4-m''-n''} \qquad \textbf{(VII)}$$

waarbij

$R^{1''}$ en $R^{2''}$ hetzelfde zijn of verschillend en elk zijn één van een halogeen, een waterstofatoom, een alkyl met 1 tot en met 20 koolstofatomen, een cycloalkyl met 3 tot en met 20 koolstofatomen, een aryl met 6 tot en met 20 koolstofatomen en een gehalogeneerde alkyl met 1 tot en met 20 koolstofatomen;

$R^{3''}$ is er één van een alkyl met 1 tot en met 20 koolstofatomen, een cycloalkyl met 3 tot en met 20 koolstofatomen, een aryl met 6 tot en met 20 koolstofatomen en een gehalogeneerde alkyl met 1 tot en met 20 koolstofatomen;

m'' en n'' zijn elk een geheel getal van 0 tot en met 3, en $m'' + n'' < 4$.

26. Gebruik van de polypropyleen volgens één van de conclusies 1 tot en met 12 of van de polypropyleen zoals bereid door gebruik te maken van een werkwijze volgens één van de conclusies 13 tot en met 25 in een ronddraai, dunne wand injectie

of gietprocessen of voor de bereiding van transparante materialen.

Rijksdienst voor Ondernemend Nederland

RAPPORT BETREFFENDE HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK

Octrooiaanvrage 2011695

Classificatie van het onderwerp[1]: C08F110/06	Onderzochte gebieden van de techniek[1]: C08F
Computerbestanden: EPODOC, WPI	Omvang van het onderzoek: Volledig
Datum van de onderzochte conclusies: 29 oktober 2013	Niet onderzochte conclusies: -

Van belang zijnde literatuur

Categorie[2]	Vermelding van literatuur met aanduiding, voor zover nodig, van speciaal van belang zijnde tekstgedeelten of figuren.	Van belang voor conclusie(s) nr.:
X	EP 0517183 A (HIMONT INC) 9 december 1992	1-8, 12-19, 25, 26
Y	* conclusies 1, 3; pagina 4, regels 36-37, 51-52, 55; pagina 5, regel 37-pagina 6, regel45; pagina 7, "general procedure"; voorbeelden; tabellen *	9-11, 20-24
	- - -	
Y	WO 2012/034357 A (CHINA PETROLEUM & CHEMICAL) 22 maart 2012 & EP 2617739 A (CHINA PETROLEUM & CHEMICAL) 24 juli 2013 * oorspronkelijke conclusies 5, 14 en 18; paragraaf [0003]; tabel 2, kolom "MI" *	9-11, 20-24
	- - -	
X	US 2008/0161513 A (YINGKOU XIANGYANG CATALYST CO) 3 juli 2008	1, 2, 26
	- - - - -	

Datum waarop het onderzoek werd voltooid: 19 januari 2015	De bevoegde ambtenaar: Dr. R.B. Boers **Octrooicentrum Nederland,** **onderdeel van Rijksdienst voor Ondernemend Nederland**

[1] Gedefinieerd volgens International Patent Classification (IPC).
[2] Verklaring van de categorie-aanduiding: zie apart blad.

Categorie van de vermelde literatuur:

X: op zichzelf van bijzonder belang zijnde stand van de techniek

Y: in samenhang met andere geciteerde literatuur van bijzonder belang zijnde stand van de techniek

A: niet tot de categorie X of Y behorende van belang zijnde stand van de techniek

O: verwijzend naar niet op schrift gestelde stand van de techniek

P: literatuur gepubliceerd tussen voorrangs- en indieningsdatum

T: niet tijdig gepubliceerde literatuur over theorie of principe ten grondslag liggend aan de uitvinding

E: octrooiliteratuur gepubliceerd op of na de indieningsdatum van de onderhavige aanvrage en waarvan de indieningsdatum of de voorrangsdatum ligt voor de indieningsdatum van de onderhavige aanvrage.

D: in de aanvrage genoemd

L: om andere redenen vermelde literatuur

&: lid van dezelfde octrooifamilie; corresponderende literatuur

AANHANGSEL BEHORENDE BIJ HET RAPPORT BETREFFENDE HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK, UITGEVOERD IN OCTROOIAANVRAGE NR. 2011695

Het aanhangsel bevat een opgave van elders gepubliceerde octrooiaanvragen of octrooien (zogenaamde leden van dezelfde octrooifamilie), die overeenkomen met octrooigeschriften genoemd in het rapport. De opgave is samengesteld aan de hand van gegevens uit het computerbestand van het Europees Octrooibureau per 29 januari 2015

De juistheid en volledigheid van deze opgave wordt noch door het Europees Octrooibureau, noch door NL Octrooicentrum gegarandeerd; de gegevens worden verstrekt voor informatiedoeleinden.

In het rapport genoemd octrooi-geschrift		datum van publicatie	overeenkomend(e) geschrift(en)		datum van publicatie
EP 0517183	A	09-12-1992	MX 9202633	A	01-12-1992
			CA 2088681	A	04-12-1992
			IT 1246614	B	24-11-1994
			WO 92/21706	A	10-12-1992
			AU 653829	B	13-10-1994
			FI 930151	A	14-01-1993
			NO 930363	A	02-02-1993
			CN 1069034	A	17-02-1993
			ZA 9203985	A	24-02-1993
			EP 0541760	A	19-05-1993
			CZ 289004	B	17-10-2001
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			PL 297841	A	13-12-1993
			JP H06-503123	A	07-04-1994
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			AT 141094	T	15-08-1996
			DK 0541760	T	02-09-1996
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			US 6228956	B	08-05-2001

In het rapport genoemd octrooi-geschrift		datum van publicatie	overeenkomend(e) geschrift(en)		datum van publicatie
WO 20/12034357	A	22-03-2012	EP 2617739	A	24-07-2013
			US 2013196847	A	01-08-2013
			KR 20130100155	A	09-09-2013
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			KR 20130100155	A	09-09-2013
US 2008161513	A	03-07-2008	CN 1670043	A	21-09-2005
			WO 20/06094445	A	14-09-2006

Rijksdienst voor Ondernemend Nederland

SCHRIFTELIJKE OPINIE

Octrooiaanvrage 2011695

Indieningsdatum: 29 oktober 2013	Voorrangsdatum: 30 oktober 2012
Classificatie van het onderwerp[1]: C08F110/06	Aanvrager: China Petroleum & Chem. Corp.

Deze schriftelijke opinie bevat een toelichting op de volgende onderdelen:

☑ Onderdeel I	Basis van de schriftelijke opinie
☑ Onderdeel II	Voorrang
☐ Onderdeel III	Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk
☐ Onderdeel IV	De aanvraag heeft betrekking op meer dan één uitvinding
☑ Onderdeel V	Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid
☐ Onderdeel VI	Andere geciteerde documenten
☐ Onderdeel VII	Overige gebreken
☑ Onderdeel VIII	Overige opmerkingen

De bevoegde ambtenaar:
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[1] Gedefinieerd volgens International Patent Classification (IPC).

Schriftelijke Opinie

Octrooiaanvraag **2011695**

Onderdeel I Basis van de schriftelijke opinie

Deze schriftelijke opinie is opgesteld op basis van de op 29 oktober 2013 ingediende conclusies.

Onderdeel II Voorrang

Deze schriftelijke opinie is opgesteld onder de aanname dat eventueel ingeroepen voorrang geldig is, tenzij hieronder anders is aangegeven. Controleren van de voorrang maakt geen deel uit van het reguliere onderzoek naar de stand van de techniek.

Onderdeel V Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid

1. Verklaring

Nieuwheid	Ja	: Conclusie(s) 9-11, 18, 20-24
	Nee	: Conclusie(s) 1-8, 12-17, 19, 25, 26
Inventiviteit	Ja	: Conclusie(s) -
	Nee	: Conclusie(s) 9-11, 18, 20-24
Industriële toepasbaarheid	Ja	: Conclusie(s) 1-26
	Nee	: Conclusie(s) -

2. Literatuur en toelichting

D1: EP 0517183 A (HIMONT INC) 9 december 1992
D2: WO 2012/034357 A (CHINA PETROLEUM & CHEMICAL) 22 maart 2012
D3: EP 2617739 A (CHINA PETROLEUM & CHEMICAL) 24 juli 2013
D4: US 2008/0161513 A (YINGKOU XIANGYANG CATALYST CO) 3 juli 2008

D1 openbaart een werkwijze voor polymerisatie van propyleen (zie conclusie 1) omvattende
1) een prepolymerisatie van propyleen in de aanwezigheid van een Ziegler-Natta katalysator (zie stap b van conclusie 1) bij een voorkeurstemperatuur van 5-50°C (zie pagina 4, regels 36-37) en een druk tussen 1,5 en 3 MPa (zie pagina 4, regel 55), waarbij 5 g tot 10% van de uiteindelijke katalyseopbrengst polymeer wordt verkregen per gram katalysator (in voorbeeld 1 rond 100g/g)
2) een polymerisatie van propyleen in de aanwezigheid van dit prepolymeer (zie stap c van conclusie 1) bij een voorkeurstemperatuur van 70-100°C (zie pagina 4, regels 51-52), een druk tussen 1,5 en 3 MPa (zie pagina 4, regel 55), met een polymerisatietijd van 54-96 minuten (zie de voorbeelden).
De Ziegler-Natta katalysator (zie conclusie 1; pagina 7, "general procedure"; pagina 5, regel 37-pagina 6, regel45) is een reactieproduct van een Ti component, een trialkyl aluminium verbinding, een organosiliconverbinding als externe elektron donor (zie conclusie 4).

Dit document openbaart daarmee de materie van conclusies 13-17, 19, 25, 26 welke daardoor niet nieuw worden bevonden.

Conclusie 18 betreft de reactieketel waarin de werkwijze bij voorkeur wordt uitgevoerd. Aangezien het hier een gebruikelijke reactieketel betreft en aangezien de beschrijving geen bijzonder effect vermeldt bij het gebruik van juist deze ketel (zie pagina 8, regels 7-10), wordt conclusie 18 gezien als een willekeurige keuze en wordt deze conclusie niet inventief bevonden.

Aangezien de werkwijze niet-nieuw dan wel niet- inventief wordt bevonden kan een product dat volgt uit die werkwijze evenmin nieuw en inventief zijn. Als de werkwijze hetzelfde is, moeten immers ook de eigenschappen van het daaruit volgende product gelijk zijn.
Aangezien de werkwijze van conclusie 13 een werkwijze voor het bereiden van het propyleen volgens een van de conclusies 1 tot en met zes is, maar ook volgens conclusies 7, 8 en 12, wordt het propyleen van conclusies 1-8 en 12 ook niet nieuw en niet inventief bevonden.

D1 openbaart niet het gebruik van een magnesium alcoholaat bij het vervaardigen van de katalysator evenmin volgt dit hieruit op een voor de hand liggende wijze. De materie van conclusies 9-11 en 20-24 wort hierdoor ten opzichte van D1 nieuw en inventief bevonden.

D3 is gepubliceerd tussen de voorrangsdatum en de indieningsdatum van de huidige aanvrage, en heeft een indieningsdatum die ligt voor de voorrangsdatum van de huidige aanvrage. Daarom behoort D3 tot de zogenaamde fictieve stand van de techniek bij de beoordeling van de huidige aanvrage. De fictieve stand van de techniek is van belang voor de nieuwheid, maar niet voor de inventiviteit van de conclusies van een octrooiaanvrage.
D2 is een zogenaamd familielid van D3 aangezien zowel D2 als D3 dezelfde twee Chinese voorrangsdocumenten inroepen. D2 is gepubliceerd op 22 maart 2012 en is daarmee een volledig tijdig document dat van belang is voor zowel de nieuwheid als de inventiviteit van de conclusies van de aanvrage. Aangezien er van mag worden uitgegaan dat D2 en D3 dezelfde uitvinding beschrijven, wordt aangenomen dat de materie die in de Engelstalige geciteerde passages uit D3 wordt beschreven ook reeds in het Chineestalige D2 zijn geopenbaard. Anders gezegd, D3 wordt gebruikt als een vertaling van het tijdige D2.

D3 (en aangenomen wordt ook het volledig tijdige D2) openbaart een polymerisatie katalysator voor olefinepolymerisatie (zie conclusies 5, 12, 14 en 18 van de oorspronkelijke set conclusies) omvattende een reactieproduct van
- alkoxymagnesium verbinding, bij voorkeur een ethoxy 2-ethylhexyloxy magnesium verbinding met 80% of meer aan ethoxy en 0,01 tot 20 gew% aan 2-ethylhexyloxy, met een D50 van 5 tot 150 micrometer en een SPAN van minder dan 1,1.
- een titanium bevattende katalysatorcomponent volgens $Ti(OR)_{4-n}X_n$ waarin X een halogeenatoom is en R een hydrocarbyl groep is
- een alkyl aluminium verbinding

- een interne elektron donor, bijvoorbeeld alkylesters
- een organo-silicone verbinding als externe elektron donor

Er wordt vermeldt dat de propyleen polymeren die worden verkregen met deze katalysatoren excellente eigenschappen hebben (zie paragraaf [0003]).

Een deskundige die het proces bekend uit D1 wil verbeteren, zal uit D3 leren dat de daaruit bekende katalysatoren polymeren met excellente eigenschappen opleveren. Een deskundige zal daarom verwachten dat als hij in het uit D1 bekende proces de katalysator bekend uit D3 zal toepassen dit voordelen zal opleveren. Het ligt dan ook voor de hand om dit te onderzoeken en te zien welke (bijzondere) eigenschappen het zo vervaardigde polymeer zal hebben.
Aangezien zulk een voor de hand liggende werkwijze dezelfde maatregelen omvat als de onderhavige conclusies 20-24, worden deze conclusies niet inventief bevonden. Evenmin kunnen de met deze niet inventieve werkwijze geproduceerde producten inventief bevonden worden. De materie van de conclusies 9-11 wordt derhalve evenmin inventief bevonden.

D4 openbaart een polypropyleen met een molecuulgewicht distributie index (MWD) van meer dan 1,9, een polydispersiteitsindex van een hoog molecuulgewichtsstaart met een moleculair gewicht distributiebreedte van meer dan 1,9, een isotactische index van meer dan 85% (zie voorbeelden 4 (MWD=3,6; PI_{HT}=2,1; II 98%) en 7 (MWD=5,3 en PI_{HT}=2,9; II 98%), waarbij de PI_{HT} is berekend met de in deze voorbeelden gegeven waarden en de formule op pagina 19 van de onderhavige aanvrage).
Dit document openbaart daarmee ten minste de materie van conclusies 1 en 2.

Onderdeel VIII Overige opmerkingen

De volgende opmerkingen met betrekking tot de duidelijkheid van de conclusies, beschrijving, en figuren, of met betrekking tot de vraag of de conclusies nawerkbaar zijn, worden gemaakt:

De gedeelten behorend bij "bij voorkeur" of "de voorkeur geniet" in conclusies 1, 2, 4-6, 8, 9, 13, 14, 16, 19, 20, 22 en 23 zijn niet beperkend voor deze conclusies.