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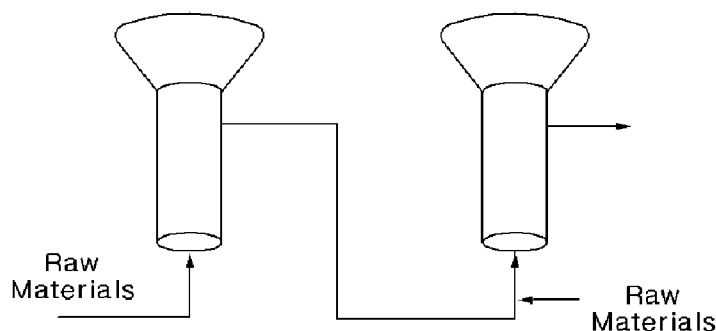
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(54) Title: PREPARATION METHOD OF RANDOM COPOLYMERS OF POLYPROPYLENE

[Fig. 1]



(57) Abstract: The preparation method of polypropylene random copolymer is disclosed, which is achieved by a bimodal polymerization method using a 2-stage continuous gas reactors for copolymerizing propylene and alpha olefin as comonomer. The polypropylene random copolymer prepared by using a bimodal gas polymerization according to the present invention has excellent physical properties such as pipe pressure resistance, processability and impact resistance, which leads to manufacturing excellent hot and cold water pipes and fittings.



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Description

Title of Invention: PREPARATION METHOD OF RANDOM COPOLYMERS OF POLYPROPYLENE

Technical Field

- [1] The present invention relates to a preparation method of random copolymers of polypropylene, and in particular to a preparation method of random copolymers of polypropylene which is achieved by a bimodal polymerization method using a 2-stage gas continuous polymerization reactor for copolymerizing propylene and alpha olefin.

Background Art

- [2] Metallic pipes are mainly used as a pressure pipe or a water heating pipe which are generally used for water supply, water heating or room warming purposes. In recent years, the use of metallic materials is being decreased, whereas a plastic material is widely used since the plastic material is cheaper as compared to the metallic material and is nontoxic and environment friendly along with its excellent chemical resistance. The durability of plastic materials is better than that of metallic materials.
- [3] Most of conventional pressure pipes are made of PVC materials, but they have environmental problems, which lead to limiting their applications. So, in recent years, a non-toxic polypropylene material is preferably used for pressure pipes.
- [4] The polypropylene can be classified into a polypropylene homopolymer, a polypropylene random copolymer and a polypropylene block copolymer. The polypropylene homopolymer has excellent chemical resistance and stiffness, so it is well applied to an industrial chemical pipe. The polypropylene block copolymer has excellent external performances with respect to an impact, stiffness and external pressure and is generally used for a buried sewerage and drainage pipe. Since the propylene homopolymer or polypropylene block copolymer does not have good pressure resistances, in particular long-term creep resistances, it is not generally used for the pressure pipes for hot and cold water supply.
- [5] Since the polypropylene random copolymer is flexible, the durability (creep resistance) for tolerating a long time pressure is excellent, which leads to an easier application for hot and cold water supply pipes.
- [6] A couple of methods for preparing polypropylene random copolymers are disclosed in the present technical fields. Among the above methods, a monomodal, which uses a single reactor, has been widely used. When actually using the above method, it is hard to control the molecular weight distribution of polymers and also hard to control the distribution of the comonomers which are included in the copolymer. So, the resulting copolymer has a certain problem for being actually applied to manufacturing the pipes

which need long-term pressure resistances (creep resistance).

- [7] There are a couple of methods which are used for preparing polypropylene homopolymer or copolymer by using a bimodal method which uses a 2-stage reactor. Among the methods, a bulk polymerization method and a slurry polymerization method are known. In the bulk method or slurry method, since a polymerization reaction occurs in liquid monomer, the reaction can be advantageously completed by even using a shorter stay time in the reactor with the help of higher catalyst activation, but there is a limit in the polymerization amount of copolymer monomer. It is hard to precisely control the amount of copolymer monomer due to the amount of low molecular solved in solvent. In the following process, a solvent treatment process is needed. Therefore, the operation cost significantly increases. The bulk or slurry polymerization method has a problem in that it is impossible to add comonomer such as ethylene more than 4 weight%.

- [8] WO 1998/58975 discloses a method for preparing bimodal type polypropylene homopolymer or copolymer, in which a slurry reactor is used as a first reactor, and a gas reactor is used as a second reactor. The monomer which is not reacted in the slurry reactor is not returned into the slurry reactor, but is directly guided into the gas reactor for thereby consuming all monomers. However, the above conventional method does not disclose how to separate hydrogen gas, non-active hydrocarbon, etc. mixed with non-reacted monomers from non-reacted monomers. Even when the above method is used, the polymer products produced in the first reaction step has low contents of copolymer monomer. So, the polypropylene homopolymer or copolymer, which is produced by using a conventional bimodal method, could be very limitedly applied to hot and cold water pipes.

Disclosure of Invention

Technical Problem

- [9] It is an object of the present invention to provide a preparation method of polypropylene random copolymers which can be applied to hot and cold water supply pipes with a long-term pressure resistance, an excellent processability and physical properties, etc. via copolymerizing propylene and alpha olefin using a 2-stage bimodal gas reactor.

Solution to Problem

- [10] To achieve the above objects, there is provided a method for preparing a propylene random copolymer which comprises a step in which a first copolymerization is performed in a 1-stage gas reactor in such a manner that propylene monomer and olefin monomer, not propylene, are mixed at 70:30~99:1 weight ratios and are reacted at 50~100°C in a pressure range of 3~45bar; and a step in which a second copoly-

merization is performed in such a manner that the production and non-reacted material produced in the first copolymerization are transferred to a 2-stage gas reactor, and in the 2-stage reactor, propylene monomer and olefin monomer, not propylene, as comonomer are mixed at 80:20~99.5:0.5 weight ratios and are reacted at 50~100°C in a pressure range of 1~30bar.

Advantageous Effects of Invention

- [11] The polypropylene random copolymer according to the present invention is characterized in that copolymers of high molecular weight and low molecular weight are widely distributed, resulting in a high Molecular Weight Distribution (Mw/Mn). In case of high molecular weight portion, the molecular weight is relatively high, and the content of copolymerization monomer is high, and in case of low molecular weight portion, the molecular weight is relatively low, and the content of copolymerization monomer is low. The polypropylene random copolymer according to the present invention is prepared in a form of composition with two types of copolymers. So, the polypropylene random copolymer according to the present invention has an excellent pressure resistance and impact resistance with the help of a lot of contents of copolymerization monomer in high molecular weight portion and also has an excellent processability with the help of copolymer in a low molecular weight portion. The present invention can be well applied to hot and cold water supply pipes which require an excellent physical performance in pressure resistance and impact resistance.

Brief Description of Drawings

- [12] Figure 1 is a view illustrating an example of a 2-stage gas reactor according to the present invention.

Best Mode for Carrying out the Invention

- [13] A method for preparing a propylene random copolymer comprises a step in which a first copolymerization is performed in a 1-stage gas reactor in such a manner that propylene monomer and olefin monomer, not propylene, are mixed at 70:30~99:1 weight ratios and are reacted at 50~100°C in a pressure range of 3~45bar; and a step in which a second copolymerization is performed in such a manner that the production and non-reacted material produced in the first copolymerization are transferred to a 2-stage gas reactor, and in the 2-stage reactor, propylene monomer and olefin monomer, not propylene, as comonomer are mixed at 80:20~99.5:0.5 weight ratios and are reacted at 50~100°C in a pressure range of 1~30bar.

Mode for the Invention

- [14] The present invention is directed to a method for preparing a random copolymer of propylene and alpha-olefin which has an excellent pressure resistance and impact resistance and processability by optimizing the contents of monomer and a copoly-

merization condition at each stage with the help of a 2-stage gas reactor.

- [15] The method for preparing a propylene random copolymer according to the present invention comprises a step in which a first copolymerization is performed in a 1-stage gas reactor in such a manner that propylene monomer and olefin monomer, not propylene, are mixed at 70:30~99:1 weight ratios and are reacted at 50~100°C in a pressure range of 3~45bar; and a step in which a second copolymerization is performed in such a manner that the production and non-reacted material produced in the first copolymerization are transferred to a 2-stage gas reactor, and in the 2-stage reactor, propylene monomer and olefin monomer, not propylene, as comonomer are mixed at 80:20~99.5:0.5 weight ratios and are reacted at 50~100°C in a pressure range of 1~30bar.
- [16] In the first copolymerization step according to the present invention, it is preferred that the ratio of contents between propylene monomer and olefin monomer, not propylene, is 80:20 ~ 99:1, and it is more preferred that the ratio is 90:10 ~ 97:3. When being out of the above ranges, it is hard to obtain a desired physical property. So, the ratio of contents is needed to be in the above range of ratios.
- [17] The reaction temperature and pressure in the first copolymerization step according to the present invention are preferably in the temperature and pressure ranges of 50~100°C and 3~45bar, respectively, and the reaction time is preferably in a range of 0.5~3hours. More preferably, the temperature is in a range of 58~70°C, and the pressure range is 18~35bar, and the reaction time is in a range of 0.7~1.5hours. When being out of the above ranges, a certain problem could rise in pipe physical properties and process operations. So, it is needed to keep the above ranges.
- [18] In a second copolymerization step according to the present invention, propylene monomer and olefin monomer, not propylene, are further added and copolymerized, and the copolymer and non-reacted monomer prepared in the 1-stage reactor are received and reacted all together.
- [19] In the present invention, the content ratio, reaction temperature, pressure and time of propylene monomer and olefin monomer, not propylene, prepared in the second copolymerization step are preferably 80:20~99.5:0.5 weight ratios, 50~100°C ranges and 1~30bar ranges, respectively. More preferably, they are 90:10~98:2 weight ratios, 60~75°C ranges and 10~20bar ranges. The reaction time is not limited, but it is preferably 0.2~2hours, and more preferably it is 0.3~1hours. When being out of the above ranges, it is hard to obtain a desired physical property of pipe, so the above ratio ranges are preferably used.
- [20] In the present invention, the olefin can unlimitedly use a certain unsaturated hydrocarbon which might be copolymerized with propylene, and olefin of C₂~C₁₀ is mainly used except for propylene. For example, ethylene, 1-butene, 1-pentene,

1-hexene, 1-heptene, 1-octene, 1-nonane, 1-decene, 4-methyl-1-pentene, 3-methyl-1-butene, vinylcyclohexane or cyclopentene can be solely used or two or more than two substances can be combined. Preferably, alpha-olefin of C₂~C₁₀ except for propylene can be used.

- [21] In the present invention, the 1-stage and 2-stage reactions are performed in the gas reactor, and are preferably performed in a sole fluidized gas reactor. In addition, the reactor is not limited to the sole fluidized gas reactor. The reactor might consist of a stirred gas reactor equipped with a mechanical stirrer. The 1- and 2- stage reactors might be one or more than one continuous gas reactors. Figure 1 is a view illustrating one example of a 2-stage gas reactor according to the present invention.
- [22] In the present invention, the polymerization reaction is performed while raising or lowering temperature. If a catalyst such as a main catalyst or a co-catalyst provides activation proper to raising the temperature in a reaction system, the catalysts used in the present invention can be unlimitedly used. Such catalysts might be Ziegler-Natta catalyst, Metallocene catalyst, etc.
- [23] When a polypropylene copolymer is manufactured by using the method according to the present invention, the Melt Flow Index (MI) of the polypropylene copolymer manufactured in the 1-stage gas reactor (under the conditions of 230°C, 2.16kg weight) is 0.001~0.30g/10minutes, and preferably 0.01~0.25g/10minutes, and the Melt Flow Index (under the conditions of 230°C, 2.16kg weight) of the final polypropylene copolymer produced in the 2-stage gas reactor is 0.1~1.0g/10minutes, and preferably 0.15~0.30g/10minutes. Since the MI of the final copolymer produced in the 2-stage polymerization reaction is lower than the MI of the copolymer produced in the 1-stage polymerization reaction, a relatively higher molecular polymer is mainly produced in the 1-stage reactor, and a relatively lower molecular polymer is produced in the 2-stage reactor.
- [24] In the 1-stage reactor, since olefin, not propylene, is used in a polymerization along with propylene for producing a random copolymer, a copolymer having more comonomer can be produced, and a copolymer with a less content of comonomer can be produced in the 2-stage reactor.
- [25] In the present invention, the content of the comonomer in the polypropylene copolymer produced in the 1-stage reactor is 3.0~20.0 weight%, and preferably 3.0~10.0 weight%, and the content of the comonomer in the final polypropylene copolymer produced in the 2-stage reactor is 3.0~15.0 weight%, and preferably, 3.5~8.0 weight%.
- [26] In the present invention, the weight ratios between the polypropylene copolymer produced in the 1-stage polymerization and the polypropylene copolymer produced in the 2-stage polymerization is 60:40~99:1, and preferably 71:29~99:1.

- [27] In the present invention, the Molecular Weight Distribution (Mw/Mn) of the final polypropylene copolymer produced in the 2-stage reactor is 4~14, and preferably 4.5~8.5.
- [28] The propylene random copolymer composition prepared according to the present invention has a density in a range of 0.890~0.910g/cm³, and the Melt Flow Index under the condition of 230°C, 2.16kg weight is 0.1~1.0g/10minutes, and the content of the copolymer monomer is 3.0~20.0 weight%, and the molecular weight distribution (Mw/Mn) is 4~15. The copolymer composition has an excellent pressure resistance and an impact resistance property, so it can be well applied to manufacturing the pressure pipes used for hot and cold water supply. Since the processability is excellent, a higher productivity can be obtained.
- [29] The preferred embodiments of the present invention will be described in more details, and the following descriptions are provided for only illustrative purposes, not limiting to the present invention.
- [30]
- [31] [Embodiment 1]
- [32] The continuous polymerization was conducted by using the 2-stage fluidized gas polymerization reactor manufactured by Dow company. Each reactor was operated via continuous processes, and 12.5tons of propylene, 500kg of ethylene and 1kg of catalyst were inputted per hour into the 1-stage reactor, and the temperature of the reactor was set at 62°C, and the polymerization was conducted under the pressure of 26.5bar for one hour. The copolymer collected in the 1-stage reactor was collected, and the Melt Flow Index (230°C, 10minutes) was measured, and the content of the ethylene comonomer was measured.
- [33] The copolymer and non-reacted substance produced in the 1-stage reaction were transferred to the 2-stage reactor, and the 2-stage reaction was performed in the 2-stage reactor after propylene and ethylene were inputted. The reaction was conducted in the 2-stage reactor for 0.5 hours at the temperature of 68°C of the reactor under the pressure of 15bar with 2.5tons of propylene and 22.5kg of ethylene being inputted per hour. The final copolymer composition produced in the 2-stage reactor was pallet-processed in the extruder, and the Melt Flow Index (230°C, 10minutes) and the ethylene comonomer and the molecular weight distribution were measured, respectively. A test piece was manufactured in a pipe shape by using a pipe extruder. A flexural modulus of elasticity, an impact resistance force, a tensile strength, pipe processability, a pressure resistance, etc. were measured. The results of the tests are shown in Table 1.
- [34]
- [35] [Comparison example 1]

- [36] The polypropylene copolymer was conducted in a monomodal method by using the 1-stage fluidized gas reactor manufactured by Dow company. As the reaction conditions, comonomer ethylene was inputted by 500kg per hour, and the other conditions are set in the same manner as the 1-stage polymer condition of the embodiment 1 of the present invention. The results of the physical measurements using the prepared copolymer are shown in Table 1.
- [37]
- [38] [Example 1 for reference]
- [39] The polypropylene random copolymer (Melt Flow Index: 0.13, the content of ethylene: 4.7 weight%) similar with the production of the 1-stage polymerization reaction prepared in the embodiment 1 and the polypropylene random copolymer (Melt Flow Index: 0.54, ethylene content: 2.7 weight%) similar with the production of the 2-stage reaction were prepared and mixed with each other, and the physical properties of the same were evaluated. The above compounding process was performed to check the possibility of bimodal polymerization in the embodiment 1. The results of the measurements of the physical properties using the prepared copolymers are shown in Table 1.
- [40]
- [41]
- [42] Physical property measurement method
- [43] (1) Melt Flow Index (MI): Measured based on ASTM D1238 at 230°C and under 2.16kg weight condition.
- [44] (2) Content of comonomer: Measured by using IR and NMR.
- [45] (3) Molecular Weight Distribution(MWD): Number average molecular weight (Mn) and Weight average molecular weight (Mw) were measured by using GPC, and the measured values were computed as the values of Mw/Mn.
- [46] (4) Flexural modulus: Measured based on ASTM 790 method. The flexural modulus were measured to check the stiffness.
- [47] (5) Impact strength (IZOD): Measured based on ASTM D256 method.
- [48] (6) Yield strength (YS), Break Strength (BS) and Elongation (EL): Measured based on ASTM D639 method.
- [49] (7) Pipe pressure property: The PSGT (Plain Strain Grooved Tensile Test) was performed based on ASTM F2018 for a long time pressure resistance of the pipe, and a short time pressure resistance of the pipes was performed based on ISO 15874.
- [50] (8) Pipe: The pipes were manufactured and evaluated by using Extruder model name LSP 63 (Screw diameter 65mm, L/D=34) manufactured by L&S company.
- [51] Table 1

[Table 1]

[Table]

Evaluation Items		Embodiment 1	Comparison Example 1	Reference Example 1
		Bimodal polymerization	Monomodal polymerization	Copolymer mixing
MI	g/10min	1-stage:0.14Final: 0.25	0.30	High molecular portion: 0.13Low molecular portion: 0.54
Content of ethylene(finally produced substance)	weight%	1-stage: 4.42-stage: 0.9Final: 3.8	3.9	High molecular portion: 4.7Low molecular portion: 2.7Final: 4.1
Flexural Modulus(FM)	kgf/cm ²	10,500	8,700	8,900
Yield strength	kgf/cm ²	280	260	270
Break strength(BS)	kgf/cm ²	240	220	290
Elongation(EL)	%	500	420	440
Impact strength(IZOD, -10°C)	Kgfc/cm	4.1	3.9	4.3
Molecular weight distribution(MWD)	Mw/Mn	6.1	4.9	-
max. Pipe Speed (Productivity)	Small diameter(Φ20*3.4T)	13m/min	9.1m/min	-
	Large diameter(Φ75*3.4T)	3.5m/min	2.8m/min	-

Pipe long time pressure re-sistance(PSGT)	5.3MPa, 95°C	broken in 832hours	broken in 268hours	-
	5.5MPa, 95°C	broken in 247hours	broken in 92hours	-
Pipe short time pressure re-sistance	16MPa, 20°C, 1 hour	Not broken in 60hours	Broken in 29hours	-

[52]

[53] As seen in the above table, in case of the embodiment 1 of the present invention, the molecular weight distribution was broadened resulting in 6.1, which had a wider molecular weight distribution as compared to the example 1 of the monomodal method which used a 1-stage reactor. This result was obtained due to the expansions of the high molecular portions and the low molecular portions via the bimodal method.

[54] The polypropylene random polymer (embodiment 1) produced by the bimodal method had a good flexural modulus (stiffness) compared with that of example 1 by the monomodal method with the help of the increase of low molecular weight portions.

[55] In the manufacture of pipes, small diameter pipes could be manufactured at 13m/min, which showed a better productivity as compared to the comparison example 1 which could be manufactured at 9.1m/min. Large diameter pipes could be manufactured at 3.5m/min as compared to the comparison example 1 which could make the pipes at 2.8m/min. So, it was possible to significantly enhance the productivity.

[56] As a result of pipe pressure resistance evaluations, the pressure resistance was better twice times in the short time pressure resistance evaluation as compared to the monomodal method. In case of the long time pressure resistance evaluation, it was conformed that the pipes were never broken for a long time, which meant that the present invention had an excellent effect with respect to pressure resistance.

[57] The impact strength, breakage strength, yield strength and elongation index were excellent in the present invention.

Industrial Applicability

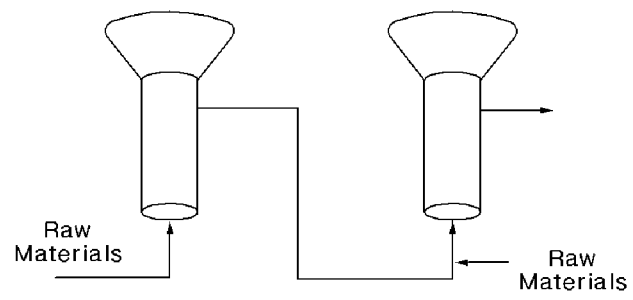
[58] As described above, the polypropylene random copolymer prepared by using the bimodal polymerization method according to the present invention has excellent performances in pressure resistance, processability and impact property, so the present invention can be well applied to manufacturing pressure resistance pipes used for hot and cold water supply.

Claims

- [Claim 1] A method for preparing a propylene random copolymer, comprising:
a step in which a first copolymerization is performed in a 1-stage gas reactor in such a manner that propylene monomer and olefin monomer, not propylene, are mixed at 70:30~99:1 weight ratios and are reacted at 50~100°C in a pressure range of 3~45bar; and
a step in which a second copolymerization is performed in such a manner that the production and non-reacted material produced in the first copolymerization are transferred to a 2-stage gas reactor, and in the 2-stage reactor, propylene monomer and olefin monomer, not propylene, as comonomer are mixed at 80:20~99.5:0.5 weight ratios and are reacted at 50~100°C in a pressure range of 1~30bar.
- [Claim 2] The method of claim 1, wherein said olefin is olefin, not propylene of C₂~C₁₀.
- [Claim 3] The method of claim 1, wherein said olefin consists of at least one selected from the group consisting of ethylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonane, 1-decene, 4-methyl-1-pentene, 3-methyl-1-butene, vinylcyclohexane and cyclopentene.
- [Claim 4] The method of claim 1, wherein said olefin is alpha-olefin, not propylene of C₂~C₁₀.
- [Claim 5] The method of claim 1, wherein the gas reactors of the 1-stage and 2-stage are fluidized gas reactor or stirred gas reactor.
- [Claim 6] The method of claim 1, wherein said 1-stage and 2-stage reactions are performed in at least one or two continuous gas reactors.
- [Claim 7] The method of claim 1, wherein the melt flow index (230°C, 2.16kg weight) of propylene copolymer produced in the 1-stage reactor is 0.001~0.30g/10minutes, and the melt flow index (230°C, 2.16kg weight) of the final polypropylene copolymer produced in the 2-stage reactor is 0.1~1.0g/10minutes.
- [Claim 8] The method of claim 1, wherein the content of comonomer in the polypropylene copolymer produced in the 1-stage reactor is 3.0~20.0 weight%, and the content of the comonomer in the final polypropylene copolymer produced in the 2-stage reactor is 3.0~15.0 weight%.
- [Claim 9] The method of claim 1, wherein the molecular weight distribution (Mw/Mn) of the final polypropylene copolymer produced in the 2-stage reactor is 4~15.

- [Claim 10] The method of claim 1, wherein the weight ratios of the copolymer produced in the 1-stage reactor and the copolymer produced in the 2-stage reactor are 60:40~99:1.
- [Claim 11] A polypropylene random copolymer composition prepared by one among claims 1 through 10 characterized in that the density of 0.890~0.910g/cm³, and the melt flow index (230°C, 2.16kg weight) is 0.1~1.0g/10 minutes, and the content of the copolymerization monomer is 3.0~20.0 weight%, and the molecular weight distribution (Mw/Mn) is 4~15.
- [Claim 12] A prepared product prepared by using the polypropylene random copolymer of claim 11.
- [Claim 13] The product of claim 12, wherein said formed product is pressure resistance pipes used for hot and cold water pipes and fittings.

[Fig. 1]



A. CLASSIFICATION OF SUBJECT MATTER***C08F 210/06(2006.01)i, C08F 2/34(2006.01)i, C08F 2/01(2006.01)i, C08J 5/00(2006.01)i***

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F 210/06; C08F 10/00; C08F 10/06; C08F 2/01; C08F 2/34; C08F 297/08; C08F 4/64; C08F 4/642; C08F 4/69; C08J 5/18

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords:propylene copolymer,two step,gas reactor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2004-0034617 A (BOREALIS TECHNOLOGY OY) 28 April 2004 See Abstract, Pages 2-3, Examples, Tables 1-2 and Claims	1-13
A	KR 10-2004-0028794 A (BOREALIS TECHNOLOGY OY) 03 April 2004 See Abstract, Examples, Tables 1-2 and Claims	1-13
A	JP 2001-310903 A (CHISSO CORP et al.) 06 November 2001 See Abstract, Paragraphs [0109]~[0120], and Claims	1-13
A	KR 10-2001-0111596 A (IDEMITSU KOSAN CO., LTD.) 19 December 2001 See Abstract and Figure 1	1-13
A	KR 10-2008-0015046 A (BOREALIS TECHNOLOGY OY) 15 February 2008 See Abstract, Paragraphs [0040]~[0069] and Examples	1-13
A	US 6573343 B1 (FOLLESTAD; ARILD) 03 June 2003 See Abstract and Tables	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

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