
(12) PATENT ABRIDGMENT (11) Document No. AU-B-81042/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 604271

(54) Title
PROCESS FOR THE POLYMERIZATION OF A LIQUID MONOMER

International Patent Classification(s)
(51)⁴ C08F 002/00 C08F 002/38 C08F 004/66

(21) Application No. : 81042/87 (22) Application Date : 28.09.87

(87) WIPO Number : WO88/02376

(30) Priority Data

(31) Number (32) Date (33) Country
911763 26.09.86 US UNITED STATES OF AMERICA

(43) Publication Date : 21.04.88

(44) Publication Date of Accepted Application : 13.12.90

(71) Applicant(s)
UNION CARBIDE CORPORATION

(72) Inventor(s)
WILLIAM STANLEY MIALKI; ALLEN NOSHAY; FATHI DAVID HUSSEIN; IAN DONALD BURDETT

(74) Attorney or Agent
CALLINAN LAWRIE, Private Bag 7, KEW VIC 3101

(56) Prior Art Documents
AU 545468 67671/81 C08F 4/66
AU 541857 66866/81 C08F 4/66

(57) Claim

1. A process for the polymerization of a liquid alpha-olefin per se or in combination with one or more other alpha-olefins, which are themselves liquids or are dissolved therein, each alpha-olefin having 2 to 12 carbon atoms, comprising the following steps effected continuously, step (a) being carried out in the liquid phase and step (b) being carried out in the gas phase:

(a) admixing a catalyst comprising (i) a catalyst precursor consisting essentially of magnesium; titanium; chlorine, bromine, or iodine; and an electron donor as an inner donor; (ii) a hydrocarbylaluminum cocatalyst; (iii) a selectivity control agent as an outer donor, said selectivity control agent being different from the electron donor, and hydrogen with the alpha-olefin(s), the ratio, by weight, of alpha-olefin(s) to catalyst

(11) AU-B-81042/87
(10) 604271

-2-

precursor being at least ~~about~~ 6000:1, in a liquid phase reactor for a residence time in the range of ~~about~~ 10 seconds to ~~about~~ 400 seconds at a temperature in the range of ~~about~~ 20°C to ~~about~~ 100°C whereby the alpha-olefin(s) are partially polymerized; and

(b) introducing the mixture from step (a) into at least one gas phase reactor at a temperature in the range of ~~about~~ 40°C to ~~about~~ 150°C in such a manner that the unpolymerized alpha-olefin is substantially polymerized.

PCT

AU-AI-81042/87
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification:

C08F 2/00, 4/64, 10/00

A1

(11) International Publication Number:

WO 88/ 02376

(43) International Publication Date:

7 April 1988 (07.04.88)

(21) International Application Number: PCT/US87/02421

(22) International Filing Date: 28 September 1987 (28.09.87)

(31) Priority Application Number: 911,763

(32) Priority Date: 26 September 1986 (26.09.86)

(33) Priority Country: US

(71) Applicant: UNION CARBIDE CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817 (US).

(72) Inventors: MIALKI, William, Stanley ; 221 Ten Eyck Road, Bridgewater, NJ 08807 (US). NOSHAY, Allen ; 66 Wellington Road, East Brunswick, NJ 08816 (US). HUSSEIN, Fathi, David ; 5094 W. Washington Street, Charleston, WV 25313 (US). BURDETT, Ian, Donald ; 11 Estill Drive, Charleston, WV 25314 (US).

(74) Agent: BRESCH, Saul, R.; Union Carbide Corporation, Law Department - E134, 39 Old Ridgebury Road, Danbury, CT 06817 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FI, FR (European patent), GB (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

A. O. J. P. 19 MAY 1988

AUSTRALIAN

21 APR '88

PATENT OFFICE

(54) Title: PROCESS FOR THE POLYMERIZATION OF A LIQUID MONOMER

(57) Abstract

A process for the polymerization of a liquid alpha-olefin per se or in combination with one or more other alpha-olefins, which are themselves liquids or are dissolved therein, each alpha-olefin having 2 to 12 carbon atoms, comprising the following steps, step (a) being carried out in the liquid phase and step (b) being carried out in the gas phase: (a) admixing a catalyst comprising (i) a catalyst precursor, which includes magnesium, titanium, chlorine, and an electron donor; (ii) a hydrocarbylaluminum cocatalyst; (iii) a selectivity control agent, said selectivity control agent being different from the electron donor; and (iv) hydrogen with the alpha-olefin(s), the ratio, by weight, of alpha-olefin(s) to catalyst precursor being at least about 6,000:1, in a liquid phase reactor for a residence time in the range of about 10 seconds to about 400 seconds at a temperature in the range of about 20°C to about 100°C whereby the alpha-olefin(s) are partially polymerized; and (b) introducing the mixture from step (a) into at least one gas phase reactor at a temperature in the range of about 40°C to about 150°C in such a manner that the unpolymerized alpha-olefin is substantially polymerized.

This document contains the amendments made under Section 49 and is correct for printing.

- 1 -

PROCESS FOR THE POLYMERIZATION OF A LIQUID MONOMER

Technical Field

This invention relates to a process for the polymerization of a liquid monomer whereby the performance of the catalyst is enhanced.

Background Art

Polymerization catalysts generally have various intrinsic limitations, which cannot be simply overcome by minor compositional adjustments. In order to overcome these limitations, a broad range of pretreatments, tailored to specific catalysts, have been proposed. These pretreatments have been found to be effective in improving catalyst activity; stereospecificity; and kinetic decay behavior; and the ability of the catalyst to survive under high polymerization temperatures (increased thermal stability).

The art is constantly seeking to identify that particular set of steps and conditions which will improve the performance of a particular catalyst in a polymerization environment.

Disclosure of the Invention

An object of this invention, therefore, is to provide a process for the polymerization of one or more monomers in a liquid pool in the presence of a catalyst comprising a catalyst precursor, usually a solid complex component, which includes magnesium, titanium, chlorine, and an electron donor; an organoaluminum compound; and a selectivity control agent whereby the activity of the catalyst is

improved as well as the other mentioned characteristics.

According to a broad form of the present invention there is provided a process for the polymerization of a liquid alpha-olefin per se or in combination with one or more other alpha-olefins, which are themselves liquids or are dissolved therein, each alpha-olefin having 2 to 12 carbon atoms, comprising the following steps effected continuously, step (a) being carried out in the liquid phase and step (b) being carried out in the gas phase:

(a) admixing a catalyst comprising (i) a catalyst precursor consisting essentially of magnesium; titanium; chlorine, bromine, or iodine; and an electron donor as an inner donor; (ii) a hydrocarbylaluminum cocatalyst; (iii) a selectivity control agent as an outer donor, said selectivity control agent being different from the electron donor, and hydrogen with the alpha-olefin(s), the ratio, by weight, of alpha-olefin(s) to catalyst precursor being at least about 6000:1, in a liquid phase reactor for a residence time in the range of about 10 seconds to about 400 seconds at a temperature in the range about 20°C to about 100°C whereby the alpha-olefin(s) are partially polymerized; and

(b) introducing the mixing from step (a) into at least one gas phase reactor at a temperature in the range of about 40°C to about 150°C in such a manner that the unpolymerized alpha-olefin is substantially polymerized.



Detailed Description

The catalyst is made up of a catalyst precursor, which includes magnesium, titanium, chlorine, and an electron donor; an organoaluminum compound, which can be referred to as a cocatalyst; and a selectivity control agent. The selectivity control agent is defined as an additive, which modifies the catalyst precursor in such a manner as to increase the overall percentage of isotactic crystalline polymer produced.

A description of one embodiment of the catalyst can be found in United States patent 4,414,132, which is incorporated by reference herein. In this case, the catalyst precursor is obtained by halogenating a magnesium compound having the formula $MgR_{2-n}X_n$ wherein R is an alkoxide or aryloxy group, each R being alike or different, X is a halogen, and $n = 0$ or 1 with a tetravalent titanium halide in the presence of a halohydrocarbon and an electron donor; contacting the halogenated product with a tetravalent titanium halide; optionally treating the resulting solid with an aromatic acid chloride; washing the halogenated product to remove unreacted titanium compounds; and recovering the solid product.

The atomic or molar ratios of catalyst components are generally as follows:

<u>Ratio</u>	<u>Broad Range</u>	<u>Preferred Range</u>
Mg to Ti	1:1 to 50:1	3:1 to 30:1
Cl to Mg	1:1 to 5:1	2:1 to 3:1
Mg to electron donor	0.1:1 to 100:1	1:1 to 60:1
Cocatalyst to Ti	10:1 to 200:1	20:1 to 100:1
Cocatalyst to selectivity control agent	0.1:1 to 100:1	0.2:1 to 50:1

Suitable halogen containing magnesium compounds that can be used to prepare the catalyst precursor are alkoxy and aryloxy magnesium halides such as isobutoxy magnesium chloride, ethoxy magnesium bromide, phenoxy magnesium iodide, cumyloxy magnesium bromide, and naphthenoxy magnesium chloride.

Magnesium compounds which can be used are magnesium dialkoxides, diaryloxides, and carboxylates having 2 to 24 carbon atoms such as magnesium di-iso-propoxide, magnesium diethoxide, magnesium dibutoxide, magnesium diphenoxide, magnesium dinaphthenoxide, and ethoxy magnesium isobutoxide, magnesium dioctanoate, and magnesium dipropionate.

Magnesium compounds having one alkoxide and aryloxy group can also be employed. Examples of such compounds are ethoxy magnesium phenoxide and naphthenoxide magnesium isoamyloxy. Also suitable are compounds having one carboxylate group and one alkoxide, aryloxy, or halide group such as ethoxy magnesium octanoate, phenoxy magnesium propionate, and chloromagnesium dodecanoate.

Suitable halides of tetravalent titanium include aryloxy- or alkoxy di- and -trihalides, such as dihexoxy titanium dichloride, diethoxy titanium dibromide, isopropoxy titanium triiodide, and phenoxy titanium trichloride; titanium tetrahalides, such as titanium tetrachloride, are preferred.

The halohydrocarbons employed can be aromatic or aliphatic. Each aliphatic halohydrocarbon preferably contains from 1 to 12 carbon atoms and at least 2 halogen atoms. The aliphatic halohydrocarbons include dibromomethane, trichloromethane, 1,2-dichloroethane, dichlorobutane, 1,1,3-trichloroethane, trichlorocyclohexane, dichlorofluoroethane, trichloropropane, trichlorofluorooctane, dibromodifluorodecane, hexachloroethane, and tetrachloroisooctane. Carbon tetrachloride and 1,1,3-trichloroethane are preferred. Aliphatic halohydrocarbons containing only one halogen atom per molecule such as butyl chloride and amyl chloride, can also be employed. Suitable aromatic halohydrocarbons include chlorobenzene, bromobenzene, dichlorobenzene, dichlorodibromobenzene, naphthyl chloride, chlorotoluene, and dichlorotoluene. Chlorobenzene is the most preferred halohydrocarbon.

Suitable electron donors, which can be used in the Mg/Ti complex (as an inner donor) or as a selectivity control agent (as an outer donor) separately or complexed with the organoaluminum compound, are ethers, mono- or polycarboxylic acid esters, ketones, phenols, amines, amides, imines, nitriles, silanes, phosphines, phosphites,

stilbenes, arsines, phosphoramides, and alcoholates. It is understood, however, that the selectivity control agent (the outer donor) must be different from the electron donor, i.e., the inner donor.

Examples are esters of carboxylic acids such as ethyl and methyl benzoate, p-methoxy ethyl benzoate, p-ethoxy methyl benzoate, p-ethoxy ethyl benzoate, ethyl acrylate, methyl methacrylate, ethyl acetate, p-chloro ethyl benzoate, p-amino hexyl benzoate, isopropyl naphthenate, n-amyl toluate, ethyl cyclohexanoate, and propyl pivalate.

Additional examples are

N,N,N',N'-tetramethylethylene diamine, 1,2,4-trimethyl piperazine, and 2,2,6,6-tetramethyl piperidine.

When the electron donor for use in preparing the catalyst precursor (the inner donor) is the preferred ethyl benzoate, the preferred electron donor for use as a selectivity control agent (the outer donor) is para-ethoxy ethyl benzoate.

The hydrocarbyl aluminum cocatalyst can be represented by the formula R_3Al wherein each R is an alkyl, cycloalkyl, aryl, or hydride radical; at least one R is a hydrocarbyl radical; two or three R radicals can be joined in a cyclic radical forming a heterocyclic structure; each R can be alike or different; and each R, which is a hydrocarbyl radical, has 1 to 20 carbon atoms, and preferably 1 to 10 carbon atoms. Further, each alkyl radical can be straight or branched chain and such hydrocarbyl radical can be a mixed radical, i.e., the radical

- 7 -

can contain alkyl, aryl, and/or cycloalkyl groups. Examples of suitable radicals are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, 2-methylpentyl, heptyl, octyl, isooctyl, 2-ethylhexyl, 5,5-dimethylhexyl, nonyl, decyl, isodecyl, undecyl, dodecyl, phenyl, phenethyl, methoxyphenyl, benzyl, tolyl, xylyl, naphthyl, naphthal, methylnaphthyl, cyclohexyl, cycloheptyl, and cyclooctyl.

Examples of suitable hydrocarbyl aluminum compounds are as follows: triisobutylaluminum, trihexylaluminum, di-isobutylaluminum hydride, dihexylaluminum hydride, isobutylaluminum dihydride, hexylaluminum dihydride, di-isobutylhexylaluminum, isobutyl dihexylaluminum, trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, trioctylaluminum, tridecylaluminum, tridodecylaluminum, tribenzylaluminum, triphenylaluminum, trinaphthylaluminum, and tritolylaluminum. The preferred hydrocarbyl aluminums are triethylaluminum, triisobutylaluminum, trihexylaluminum, di-isobutylaluminum hydride, and dihexylaluminum hydride.

The acid halide mentioned above is the compound corresponding to the ester compound used as the inner electron donor. Preferably, the halide is a chloride or bromide. The acid halide can contain 7 to 22 carbon atoms and one or more aromatic rings.

The first step is a liquid monomer polymerization, i.e., a liquid phase polymerization, in which, ^{preferably} no more than about 10 percent by weight of



- 8 -

the polymer produced in subject process is formed. This first step (step (a)) can be carried out in a conventional reactor constructed of a material inert to the reaction. It is preferably carried out in a loop reactor. The reactor is filled with a liquid containing one liquid alpha-olefin by itself or in combination with one or more other alpha-olefins, which are themselves liquids or gases dissolved in the liquid, each alpha-olefin having 2 to 12 carbon atoms. While the preferred liquid monomer is liquid propylene other liquid or soluble alpha-olefins, which can be used are 1-butene, 1-hexene, or 1-dodecene. Examples of alpha-olefins which can be dissolved in the liquid pool are ethylene and propylene.

The catalyst precursor, in slurry form, together with the cocatalyst, selectivity control agent, alpha-olefin, and hydrogen are continuously fed into the reactor in the desired ratios.

The ratio, by weight, of alpha-olefin(s) to catalyst precursor in the first reactor, i.e., the first step, is at least about 6,000:1 and is preferably in the range of about 9,000:1 to about 50,000:1; the residence time in the first reactor is in the range of about 10 to about 400 seconds and preferably about 40 to about 200 seconds; the temperature maintained in the first reactor is about 20°C to about 100°C and is preferably about 40°C to about 80°C; the pressure is sufficient to keep the monomer(s) liquid, about 150 psig to about 800 psig and preferably about 200 psig to about 600 psig; the mole ratio of hydrogen to alpha-olefin(s) is in the

range of about 0.0005:1 to about 0.01:1 and is preferably about 0.001:1 to about 0.005:1; the catalyst, hydrogen and monomer(s) are fed into the first reactor at a rate sufficient to produce about 50 to about 2000 pounds of polymer per pound of catalyst precursor and preferably about 100 to about 1500 pounds of polymer per pound of catalyst precursor.

The mixture of catalyst and liquid monomer(s) is continuously circulated during the residence period and continuously discharged into a gas phase reactor, preferably a fluidized bed reactor, thereafter. Conventional circulating means such as the impeller pump mentioned in the examples are used. It should be emphasized that in the preferred mode there is essentially no delay between the first and second steps; however, a ramping technique can be used between steps, if desired, whereby the mixture of catalyst and liquid monomer(s) passes through a temperature gradient in which the temperature of the mixture is gradually increased from the first reactor temperature to the second reactor temperature in a stepwise fashion. This gradual ramp should be accomplished, however, in a total elapsed time of no more than about 400 seconds. In addition to the mixture from step (a), which includes catalyst, alpha-olefin, and polymerized alpha-olefin, alpha-olefin monomer(s) and hydrogen can also be introduced into the gas phase reactor.

The gas phase reactor can be the fluidized bed reactor described in United States Patent

- 10 -

4,482,687 or another conventional reactor for the gas phase production of, for example, polypropylene or propylene copolymers. The bed is usually made up of the same granular resin that is to be produced in the reactor. Thus, during the course of the polymerization, the bed comprises formed polymer particles, growing polymer particles, and catalyst particles fluidized by polymerizable and modifying gaseous components introduced at a flow rate or velocity sufficient to cause the particles to separate and act as a fluid. The fluidizing gas is made up of the initial feed, make-up feed, and cycle (recycle) gas, i.e., monomer and, if desired, modifiers and/or an inert carrier gas.

The essential parts of the reactor are the vessel, the bed, the gas distribution plate, inlet and outlet piping, a compressor, a cycle gas cooler, and a product discharge system. In the vessel, above the bed, there is a velocity reduction zone, and in the bed, a reaction zone. Both are above the gas distribution plate.

Variations in the reactor can be introduced if desired. One involves the relocation of the cycle gas compressor from upstream to downstream of the cooler and another involves the addition of a vent line from the top of the product discharge vessel (stirred product tank) back to the top of the first reactor to improve the fill level of the product discharge vessel.

The fluidized bed reactor used in the second step is operated at a temperature in the range of about 40°C to about 150°C and preferably

about 60°C to about 120°C and a pressure of, ^{preferably} about 100 psig to about 700 psig and ^{more} preferably about 250 psig to about 550 psig. The velocity of the fluidizing gas is in the range of about 0.1 to about 3.0 feet per second and preferably about 0.5 to about 2.0 feet per second. The mole ratio of hydrogen to alpha-olefin(s) in the fluidized bed reactor is in the range of about 0.005:1 to about 0.2:1 and is preferably in the range of about 0.01:1 to about 0.1:1.

Where it is desired to produce a homopolymer such as polypropylene or a random copolymer such as a propylene/ethylene random copolymer, one fluidized bed reactor is used. In the case of impact grade copolymers, a second fluidized bed reactor is needed. In all cases the reactors, i.e., the loop reactor in which the first step is carried out, the second reactor, i.e., the fluidized bed reactor, and, if required, a third reactor, again a fluidized bed, are operated continuously, in-line.

The invention is illustrated by the following examples:

EXAMPLES 1 - 6

A loop reactor having a jacketed section for heat removal is filled with liquid propylene. To this reactor is charged a prepared catalyst precursor having the following approximate composition: $\text{TiCl}_4 \cdot 12 \text{MgCl}_2 \cdot 2 \text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$. The catalyst precursor is in slurry form and conveyed to the loop reactor using liquid propylene. The weight ratio of liquid propylene to catalyst precursor is



- 12 -

12,500:1.2 (10,417:1). A cocatalyst, triethylaluminum, and a selectivity control agent, para-ethoxy ethyl benzoate, in a mole ratio of about 3:1 are fed into the reactor at the same time as the catalyst precursor. The atomic ratio of aluminum to titanium is 36. Hydrogen is also fed into the loop reactor in a mole ratio of hydrogen to liquid propylene of 0.002:1. The pressure in the loop reactor is 550 psig; the temperature is about 55°C; there are 1300 pounds of polypropylene formed per pound of catalyst precursor; the flow rate through the loop reactor is about 12,500 pounds of mixture of catalyst and liquid propylene per hour; and the residence time in the loop reactor is 95 seconds.

The mixture is continuously circulated through the loop reactor by means of a single semi-open impeller centrifugal pump; and is continuously discharged from the loop reactor into a fluidized bed reactor where the main polymerization takes place. The conditions under which the fluidized bed reactor is operated are approximately as follows:

temperature: 67°C

pressure: 490 psig

flow rate: about 12,500 pounds per hour of
mixture of catalyst and liquid
propylene from the loop reactor
plus 8000 pounds per hour of
propylene fed directly to the
fluidized bed reactor

fluidizing gas velocity: 0.8 foot per
second

Hydrogen is also fed into the fluidized bed reactor in a mole ratio of hydrogen to propylene of 0.02:1.

No additional catalyst precursor, cocatalyst, or selectivity control agent are added to the fluidized bed reactor.

The example is repeated omitting the first step. In this case, the catalyst and propylene are charged directly into the fluidized bed reactor.

The two step and the one step examples are repeated twice.

The Table shows the following variables and results:

1. Al/Ti atomic ratio
2. Xylene solubles: since non-crystalline polypropylene is soluble in xylene and crystalline polypropylene, which is preferred, is not, the measure of xylene solubles is an indication of how much crystalline polypropylene is being produced. The value is given in percent by weight based on the total weight of the polymer. A value of less than 6 percent is commercially desirable.
3. Total productivity with first step is given in thousands of pounds of polymer per pound of titanium. This shows the amount of polymer produced by the two step process, i.e., the invention.
4. Productivity without first step is also given in thousands of pounds of polymer per pound of titanium. This indicates productivity using only the fluidized bed reactor.
5. Percent productivity improvement gives the percentage of productivity increase of the

- 14 -

fourth column over the fifth column, i.e., example 1 is compared with example 2; example 3 with example 4; and example 5 with example 6.

Note: The data in the table demonstrate that the use of the first step (step (a)) results in a substantial improvement in catalyst polymerization productivity. This increased productivity is a reflection of improved catalyst activity, stereospecificity, kinetic decay behavior, and thermal stability.

TABLE

<u>Example</u>	<u>Al/Ti</u>	<u>Xylene Solubles</u>	<u>Catalyst productiv- ity With 1st Step</u>	<u>Catalyst productiv- ity without 1st Step</u>	<u>% Catalyst productivity Improvement</u>
1	36	3.4	690	-	24.3
2	36	3.4	-	555	-
3	35	3.7	740	-	25.9
4	35	3.7	-	588	-
5	31	2.8	625	-	37.4
6	31	2.8	-	455	-

16

WO 88/02376

PCT/US87/02421

AMENDED CLAIMS

[received by the International Bureau on 18 April 1988 (18.04.88):
original claims 1 and 5 amended, remaining claims unchanged (2 pages)]

1. A process for the polymerization of a liquid alpha-olefin per se or in combination with one or more other alpha-olefins, which are themselves liquids or are dissolved therein, each alpha-olefin having 2 to 12 carbon atoms, comprising the following steps effected continuously, step (a) being carried out in the liquid phase and step (b) being carried out in the gas phase:

(a) admixing a catalyst comprising (i) a catalyst precursor consisting essentially of magnesium; titanium; chlorine, bromine, or iodine; and an electron donor as an inner donor; (ii) a hydrocarbylaluminum cocatalyst; (iii) a selectivity control agent as an outer donor, said selectivity control agent being different from the electron donor, and hydrogen with the alpha-olefin(s), the ratio, by weight, of alpha-olefin(s) to catalyst precursor being at least ~~about~~ 6000:1, in a liquid phase reactor for a residence time in the range of ~~about~~ 10 seconds to ~~about~~ 400 seconds at a temperature in the range of ~~about~~ 20°C to ~~about~~ 100°C whereby the alpha-olefin(s) are partially polymerized; and

(b) introducing the mixture from step (a) into at least one gas phase reactor at a temperature in the range of ~~about~~ 40°C to ~~about~~ 150°C in such a manner that the unpolymerized alpha-olefin is substantially polymerized.

2. The process defined in claim 1 wherein at least one liquid alpha-olefin is liquid propylene.

3. The process defined in claim 2 wherein ethylene is dissolved in the liquid propylene.



4. The process defined in claim 1, wherein the atomic ratio of aluminum to titanium is in the range of 10:1 to 200:1.

5. The process defined in claim 4, wherein the molar ratio of cocatalyst to selectivity control agent is in the range of 0.1:1 to 100:1.

6. The process defined in claim 1, wherein, in step (a), the ratio, by weight, of alpha-olefin(s) to catalyst precursor is in the range of 9,000:1 to 50,000:1; the residence time is in the range of 40 seconds to 200 seconds; and the temperature is in the range of 40°C to 80°C.

7. The process defined in claim 6, wherein the electron donor is ethyl benzoate and the selectivity control agent is para-ethoxy ethyl benzoate.

8. A process for the polymerization of a liquid alpha-olefin per se or in combination with one or more other alpha-olefin(s), which are themselves liquids or are dissolved therein, each alpha-olefin having 2 to 12 carbon atoms, which process is substantially as herein described with reference to any one of the Examples.

9. The product whenever prepared by the process of any one of claims 1 to 8.

D A T E D this 5th day of September 1990.

UNION CARBIDE CORPORATION

By their Patent Attorneys:

CALLINAN LAWRIE

Michael J. Houlahan.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 87/02421

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 F 2/00; C 08 F 4/64; C 08 F 10/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ?		
Classification System	Classification Symbols	
IPC ⁴	C 08 F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB, A, 2068981 (CHISSO CORP.) 19 August 1981, see the claims; page 5, lines 1-13; examples 20-22	1-7
X	GB, A, 2070630 (CHISSO CORP.) 9 September 1981, see the claims; page 6, lines 29-36; examples 23-25	1-7
A	EP, A, 0019330 (SHELL) 26 November 1980, see the claims	1
A	EP, A, 0003228 (CHEM. WERKE HÜLS) 8 August 1979, see the claims	

* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
18th January 1988	26 FEB 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	P. C. VAN DER PUTTEN	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 8702421

SA 19172

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 10/02/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2068981	19-08-81	BE-A- 887377	01-06-81
		FR-A, B 2475050	07-08-81
		NL-A- 8100534	01-09-81
		JP-A- 56110707	02-09-81
		DE-A, C 3103990	03-12-81
		AU-A- 6686681	13-08-81
		US-A- 4368304	11-01-83
		CA-A- 1151142	02-08-83
		AU-B- 541857	24-01-85
		DE-C- 3153128	03-12-87
GB-A- 2070630	09-09-81	BE-A- 887678	15-06-81
		FR-A, B 2476656	28-08-81
		NL-A- 8100824	16-09-81
		JP-A- 56120712	22-09-81
		DE-A, C 3107334	10-12-81
		US-A- 4309521	05-01-82
		AU-A- 6767181	03-09-81
		CA-A- 1142698	08-03-83
		US-A- 4514513	30-04-85
		AU-B- 545468	18-07-85
EP-A- 0019330	26-11-80	JP-A- 55152710	28-11-80
		AU-A- 5830780	20-11-80
		CA-A- 1141093	08-02-83
		US-A- 4393182	12-07-83
		US-A- 4400302	23-08-83
		US-A- 4414132	08-11-83
		AU-B- 536252	03-05-84
EP-A- 0003228	08-08-79	DE-A- 2803280	03-01-80

EP-A- 0003228

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82