

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
1 April 2004 (01.04.2004)

PCT

(10) International Publication Number
WO 2004/026925 A1

- (51) International Patent Classification⁷: **C08F 210/06**, 4/642
- (21) International Application Number: PCT/US2003/028873
- (22) International Filing Date: 12 September 2003 (12.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/411,778 17 September 2002 (17.09.2002) US
- (71) Applicant (*for all designated States except US*): **DOW GLOBAL TECHNOLOGIES INC.** [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **ARRIOLA, Daniel, J.** [US/US]; 2100 East Mier Road, Midland, MI 48642 (US). **BOKOTA, Marilyn** [US/US]; 4431 West Lange, Beaverton, MI 48612 (US). **TIMMERS, Francis, J.** [US/US]; 4605 Lund Drive, Midland, MI 48642 (US).
- (74) Agent: **DELINE, Douglas, N.**; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 2004/026925 A1

(54) Title: IMPROVED PROCESS FOR MANUFACTURE OF POLYMERS

(57) Abstract: A process for preparing interpolymers of ethylene and one or more C₃₋₈ olefin monomers comprising contacting a monomer mixture comprising ethylene and one or more C₃₋₈ olefin monomers with a catalyst composition comprising a Group 4 metal complex of a polyvalent, Lewis base ligand under addition polymerization conditions.

IMPROVED PROCESS FOR MANUFACTURE OF POLYMERS

Cross Reference Statement

This application claims the benefit of U.S. Provisional Application No. 60/411,778, filed
5 September 17, 2002.

Background Of The Invention

The present invention relates to a process for preparing olefin interpolymers having
improved efficiency and capable of preparing polymers having increased molecular weights. The
10 resulting interpolymers, including polypropylene, are well known commercially and may be
usefully employed in the preparation of solid articles such as moldings, films, sheets and foamed
objects by molding, extruding or other processes.

The manufacture of olefin interpolymers by use of catalysts comprising Group 4 metal
amide complexes and halide or alkyl metal derivatives thereof has been previously taught in
15 US-A-5,312,938, US-A-5,597,935, US-A-5,861,352, US-A-5,880,302, US-A-6,020,444, and
US-A-6,232,256, and elsewhere. In US-A-6,320,005 and US-A-6,103,657 certain transition metal
amine donor complexes for use as components of olefin polymerization catalysts were disclosed.
In WO 02/38628 additional description of such Group 4 metal complexes containing "spectator
ligands" such as amino- substituted cyclic amine compounds were disclosed.

20

Summary Of The Invention

According to the present invention there is now provided a process for preparing
interpolymers of ethylene and one or more C₃₋₈ olefin monomers comprising contacting a
monomer mixture comprising ethylene and one or more C₃₋₈ olefin monomers with a catalyst
25 composition comprising a Group 4 metal complex of a polyvalent, Lewis base ligand under
addition polymerization conditions.

Preferably the ethylene is present in the polymerization in a minor amount sufficient to
improve the molecular weight of the resulting interpolymers or to improve the efficiency of the
polymerization process, and preferably to obtain both objectives, but not in an amount that
30 substantially alters the tacticity of the resulting C₃₋₈ interpolymers. In particular, it has been
discovered that if a minor proportion of ethylene is present in such polymerizations, the resulting
polymers possess substantially the same properties as a polymer in which no polymerized
ethylene is present, but the same can be prepared having much improved molecular weights.
Moreover, the process for preparing such interpolymers is more efficient, compared to processes

in which ethylene is absent. Thus, according to one aspect of the invention, it is desired to utilize ethylene not for the preparation of elastomeric or amorphous copolymers, but rather in order to improve the molecular weight of the polymer and/or the catalytic efficiency of the polymerization process.

5 In a further embodiment of the present invention there is provided a process for preparing interpolymers of ethylene and one or more C₃₋₈ olefin monomers comprising contacting a monomer mixture comprising ethylene and one or more C₃₋₈ olefin monomers, wherein said ethylene is present in the mixture in an amount from 0.1 to 10 percent based on total monomer weight, with a catalyst composition comprising a Group 4 metal complex of a polyvalent, Lewis
10 base ligand under addition polymerization conditions:

Detailed Description Of The Invention

 All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1999. Also, any references
15 to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference), especially with respect to the disclosure of synthetic techniques and
20 general knowledge in the art. The term "comprising" when used herein with respect to a composition, mixture or process is not intended to exclude the additional presence of any other compound, component or step.

 By the term "interpolymer" herein is meant any form of polymer, including graft or block polymers, that includes in polymerized form two or more monomers. By the term "random
25 distribution" as used herein, is meant that the ethylene functionality resulting from polymerization of the ethylene monomer is distributed within each polymer chain in a random or nearly random, for example, non-block, manner (intrachain distribution). By the term "uniform distribution" is meant that the foregoing ethylene functionality is equally or nearly equally distributed among different polymer chains (that is, homogeneous interchain distribution).

30 Quantification of ethylene content in the interpolymers of the invention may be achieved by the use of any suitable analytical technique, including ¹³C NMR-, and IR- spectroscopic analysis of the interpolymer. Interchain distribution within the interpolymers may be measured by a polymer fractionation technique, followed by analysis of the various polymer fractions, using one of the foregoing techniques. Examples of suitable fractionation techniques include

Temperature Rising Elution Fractionation (TREF), Analytical Temperature Rising Elution Fractionation (ATREF) or high pressure liquid chromatography (HPLC).

TREF analysis is a well known method of fractionation that has been published in the open literature over the past 15 years. ATREF is a similar technique for fractional analysis of olefin polymers capable of fractionating semi-crystalline polymers as a function of crystallization temperature while simultaneously estimating the molecular weight of the fractions. It has been described in US-A-4,798,081, as well as in "Determination of Short-Chain Branching Distributions of Ethylene copolymers by Automated Analytical Temperature Rising Elution Fractionation" (Auto-ATREF), *J. of Appl Pol Sci: Applied Polymer Symposium* 45, 25-37 (1990). The primary difference between ATREF and TREF is that the ATREF technique is done on a small scale and fractions are not actually isolated. Instead, a typical liquid chromatographic (LC) mass detector, such as an infrared single frequency detector, is used to quantify the crystallinity distribution of a polymer as a function of elution temperature. This distribution can then be transformed to any number of alternative domains such as comonomer distribution. This transformed distribution can then be interpreted according to a structural variable like comonomer content.

To obtain ATREF data, a commercially available viscometer especially adapted for LC analysis, such as a Viskotek™ is coupled with the IR mass detector. Together these two LC detectors can be used to calculate the intrinsic viscosity of the ATREF eluant. The viscosity average molecular weight of a given fraction can then be estimated using appropriate Mark Houwink constants, the corresponding intrinsic viscosity, and suitable coefficients to estimate the fractions concentration (dl/g) as it passes through the detectors. Thus, a typical ATREF report will provide the weight fraction polymer and viscosity average molecular weight as a function of elution temperature.

The molecular weight partitioning factor, M_{pf} , characterizes the ratio of the average molecular weight of the fractions with high ethylene comonomer content to the average molecular weight of the fractions with low ethylene comonomer content. Higher and lower ethylene contents polymers are defined as being below or above the median elution temperature of the TREF concentration plot respectively. That is, the TREF data is divided into two parts of equal weight. M_{pf} is calculated from the following equation:

$$M_{pf} = \frac{\frac{\sum_{i=1}^n w_i \cdot M_i}{\sum_{i=1}^n w_i}}{\frac{\sum_{j=1}^m w_j \cdot M_j}{\sum_{j=1}^m w_j}},$$

where: M_i is the viscosity average molecular weight and w_i is the normalized weight fraction as determined by ATREF for the n data points in the fractions below the median elution temperature. M_j is the viscosity average molecular weight and w_j is the normalized weight fraction as determined by ATREF for the m data points in the fractions above the median elution temperature. Only those weight fractions, w_i or w_j , which have associated viscosity average molecular weights greater than zero are used to calculate M_{pf} . For a valid calculation, it is required that n and m are greater than or equal to 3.

Randomness, or the distribution of monomer functionality within a chain, can be calculated based on the various reactivity ratios for the catalyst with respect to the various comonomers. For a polymerization of two monomers, as a most useful example, the reactivity ratios, r , for each monomer may be calculated based on two indices, i and j , where k_{ij} is the rate constant for the most recently incorporated monomer i , with incoming monomer i or j during catalysis, with the reactivity ratio defined according to the formula: $r_{ij} = k_{ii}/k_{ij}$. Thus, for two monomers, identified as 1 and 2, respectively, $r_{12} = k_{11}/k_{12}$ and $r_{21} = k_{22}/k_{21}$. A random distribution of monomers throughout the copolymer chain is achieved when $r_{12} \cdot r_{21}$ is approximately equal to 1. Preferred interpolymers of the invention are those wherein the ethylene randomness meets the requirement of: $0.1 < r_{12} \cdot r_{21} < 10.0$, more preferably $0.5 < r_{12} \cdot r_{21} < 2$, most preferably $0.75 < r_{12} \cdot r_{21} < 1.5$. Highly preferably, all comonomers are uniformly and randomly distributed within the polymer chains, or are nearly uniformly and randomly distributed. For a highly uniform polymer, the intrachain distribution or homogeneity of the polymer can also be determined using ^{13}C NMR spectroscopy, according to known techniques.

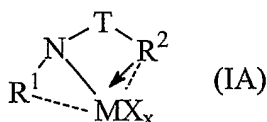
As used herein the term "long chain branching" refers to pendant oligomeric, hydrocarbyl-, groups attached to the polymeric chain, which groups have a length greater than $m-2$ carbons, wherein m is the number of carbons in the largest α -olefin of the ethylene/ C_{3-8} olefin mixture. Long chain branching generally is thought to result from the reincorporation of addition polymerizable compounds generated as a result of β -hydride elimination, or other vinyl group

generating process. Generally, the present invention does not result in the generation of substantial quantities of long chain branches.

Several techniques for measuring the extent of long chain branching in a copolymer already exist. Principle analytical techniques include those based on ^{13}C NMR analysis, optionally coupled with low angle laser light scattering or similar particle size measuring technique. Additionally, it is possible to arrive at an estimate of short chain branches, that is, branches due to the C_{3-8} comonomer remnant, by preparation of a control copolymer using a labeled monomer, such as ^{13}C enriched 1-octene or ethylene, under the assumption that a similar level of branch distribution will exist in copolymers made under comparative conditions utilizing unmodified monomers. The level of long chain branching is thereafter determined by subtraction. Preferred polymers according to the present invention contain less than 0.3 long chain branches per 10,000 carbons, preferably less than 0.1 long chain branches per 10,000 carbons.

Most preferred olefin mixtures for use herein are mixtures of ethylene and propylene, containing from 0.5 to 5.0, most preferably from 0.5 to 1.0, weight percent ethylene. Uniquely, according to the present invention, it is believed, without wishing to be bound by such belief, that the ethylene in the monomer mixture does not operate as a chain transfer agent during the polymerization, thereby terminating the polymerization and reducing the molecular weight of the resulting polymers, as often occurs using other catalyst systems. Furthermore, it is believed that ethylene causes the rate of other chain transfer events to decrease, thereby resulting in production of higher molecular weight polymers compared to polymers formed in the absence of ethylene. Thus, the preparation of higher molecular weight polymers in a high efficiency process by adding a small quantity of ethylene to a polymerization mixture comprising one or more C_{3-8} olefins, especially propylene, is unexpected and contrary to the normal results achieved with catalyst compositions based on Group 4 metal complexes containing delocalized π -bonded ligand groups, especially metallocenes.

Examples of suitable metal complexes of polyvalent ligands for use in the present invention include Group 4 metal derivatives, especially hafnium derivatives of hydrocarbylamine substituted heteroaryl compounds of the formula $\text{R}^1\text{HN-T-R}^2$ (I), said complexes corresponding to the formula:



30

wherein

R^1 is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen;

T is a divalent bridging group of from 1 to 20 atoms other than hydrogen, preferably a mono- or di- C_{1-20} hydrocarbonyl substituted methylene or silane group, and

5 R^2 is a C_{6-20} heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group,

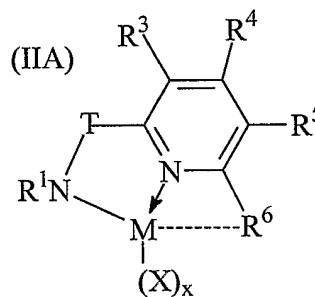
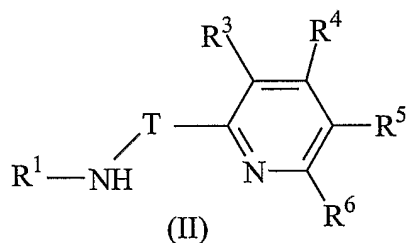
and in the metal complex, M is the Group 4 metal, preferably hafnium,

X is an anionic, neutral or dianionic ligand group,

x is a number from 0 to 5 indicating the number of such X groups, and

10 bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

Preferred complexes are those wherein ligand formation results from hydrogen elimination from the amine group and optionally from the loss of one or more additional groups, especially from R^2 . In addition, electron donation from the Lewis base functionality, preferably an electron pair, provides additional stability to the metal center. Preferred examples of the
15 foregoing polyfunctional Lewis base compounds and the resulting metal complexes correspond to the formulas:



, wherein

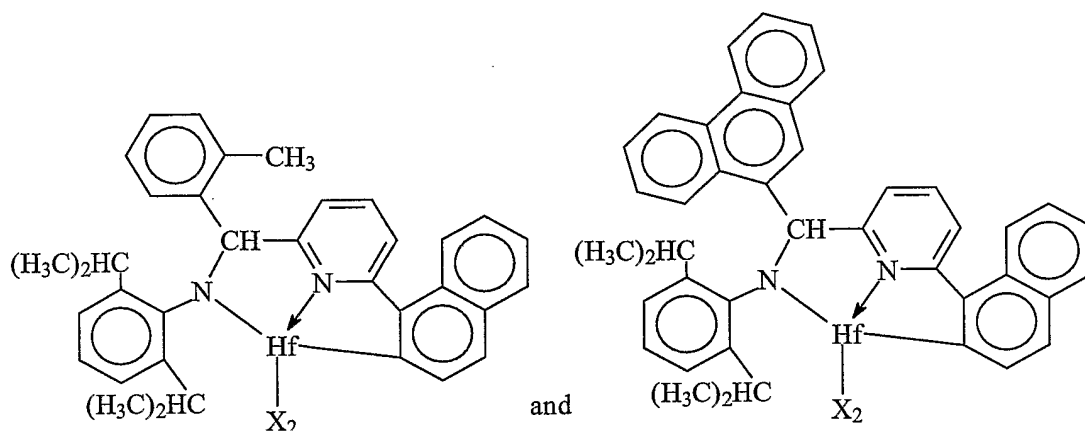
M, X, x, R^1 and T are as previously defined,

20 R^3 , R^4 , R^5 and R^6 are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent R^3 , R^4 , R^5 or R^6 groups may be joined together thereby forming fused ring derivatives, and

bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

25 More preferred examples of the foregoing difunctional Lewis base compounds and metal complexes correspond to the formula:

Most highly preferred examples of metal complexes for use according to the present invention are complexes of the following formulas:



wherein X each occurrence is halide, N,N-dimethylamido, or C₁₋₄ alkyl, and preferably each occurrence X is methyl.

Examples of metal complexes usefully employed according to the present invention include:

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido); and

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride.

Under the reaction conditions of the present invention, it has been discovered that the hydrogen of the 2-position of the α -naphthalene group substituted at the 6-position of the pyridin-2-yl group is subject to elimination, thereby uniquely forming metal complexes wherein the metal is covalently bonded to both the resulting amide group and to the 2-position of the α -naphthalenyl group, as well as stabilized by coordination to the pyridinyl nitrogen atom through the electron pair of the nitrogen atom.

The foregoing metal complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the Group 4 metal and the neutral polyfunctional ligand source. The complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding Group 4 metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum, as disclosed in WO 02/38628. Other techniques may be used as well.

The resulting Group 4 metal complexes are activated to form the actual catalyst composition by combination with a cocatalyst, preferably an aluminoxane, a cation forming cocatalyst, or a combination thereof. The mixture of monomers may be contacted with the active catalyst composition according to any suitable polymerization conditions. Also, the quantity of ethylene during the polymerization may be varied or even eliminated, provided that during some portion of the polymerization a mixture comprising ethylene and one or more C₃₋₈ olefins is present. The process is characterized by use of temperatures typically from 25 to 50 °C and pressures from atmospheric to 10 MPa. Hydrogen may be employed as a chain transfer agent for molecular weight control according to known techniques if desired. Of course, if the objective of attaining polymers having increased molecular weight is desired, no chain transfer agent is employed.

Suitable alumoxanes for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane, triisobutyl aluminum modified methylalumoxane, or isobutylalumoxane; neutral Lewis acid modified polymeric or oligomeric alumoxanes, such as the foregoing alkylalumoxanes modified by addition of a C₁₋₃₀ hydrocarbyl substituted Group 13 compound, especially a tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compound, or a halogenated (including perhalogenated) derivative thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially a perfluorinated tri(aryl)boron compound or a perfluorinated tri(aryl)aluminum compound.

The Group 4 metal complexes may also be rendered catalytically active by combination with a cation forming cocatalyst, such as those previously known in the art for use with Group 4 metal olefin polymerization complexes. Suitable cation forming cocatalysts for use herein include neutral Lewis acids, such as C₁₋₃₀ hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluoro-phenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially

the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, or ferrocenium-, lead- or silver salts of compatible, noncoordinating anions; and combinations of the foregoing cation forming cocatalysts and techniques. The foregoing activating cocatalysts and activating techniques have been previously
5 taught with respect to different metal complexes for olefin polymerizations in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, US-A-5,321,106, US-A-5,721,185, US-A-5,350,723, US-A-5,425,872, US-A-5,625,087, US-A-5,883,204, US-A-5,919,983, US-A-5,783,512, WO 99/15534, and WO99/42467.

As in other similar polymerizations, it is highly desirable that the monomers and solvents
10 employed be of sufficiently high purity that catalyst deactivation does not occur. Any suitable technique for monomer purification such as devolatilization at reduced pressures, contacting with molecular sieves or high surface area alumina, or a combination of the foregoing processes may be employed.

Purification of the resulting polymer to remove entrained catalyst and cocatalyst may also
15 be desired by the practitioner. Such contaminants may generally be identified by residues of ash on pyrolysis of the polymer that are attributable to catalyst or cocatalyst metal values. A suitable technique for removing such compounds is by solvent extraction, for example, extraction utilizing hot, high boiling chlorinated solvents, acids or bases such as caustic followed by filtration.

A support may be optionally present in the catalyst formulation especially in a gas phase
20 or slurry polymerization. Suitable supports include any inert, particulate material, but most suitably is a metal oxide, preferably alumina, silica, or an aluminosilicate material. Suitable particle sizes are from 1 to 1000 μm , preferably from 10 to 100 μm . Most desired supports are calcined silica, which may be treated to reduce surface hydroxyl groups by reaction with a silane, or similar reactive compound. Any suitable means for including such support in the catalyst
25 formulation may be used, such as by dispersing the components in a liquid and contacting the same with the support and thereafter drying, by spraying, or coating the support with such liquid and thereafter removing the liquid, or by coprecipitating the cocatalyst and a support material from a liquid medium.

The polymerization is desirably carried out as a continuous polymerization, in which
30 catalyst components, monomers, and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to the reaction zone and polymer product continuously removed therefrom. Within the scope of the terms "continuous" and "continuously" as used in this context are those processes in which there are intermittent additions of reactants

and removal of products at small regular intervals, so that, over time, the overall process is approximately continuous.

In one embodiment of operation, the polymerization is conducted in a continuous solution polymerization system, including such a system comprising one or more polymerization reactors. In another embodiment two reactors connected in series or parallel are employed. In one reactor a relatively high molecular weight product (Mw from 200,000 to 600,000, more preferably 300,000 to 500,000) is formed while in the second reactor a product of a relatively low molecular weight (Mw 50,000 to 2300,000) is formed. The final product is a blend of the two reactor effluents which are combined prior to devolatilization to result in a uniform blend of the two polymer products. Such a dual reactor process allows for the preparation of products having improved properties. In a preferred embodiment the reactors are connected in series, that is effluent from the first reactor is charged to the second reactor and fresh monomer, solvent and hydrogen is added to the second reactor. Reactor conditions are adjusted such that the weight ratio of polymer produced in the first reactor to that produced in the second reactor is from 20:80 to 80:20. In addition the temperature of the second reactor is controlled to produce the lower molecular weight product.

The polymerization process of the present invention can also be employed to advantage in a gas phase copolymerization process. Such processes are used commercially on a large scale for the manufacture of polypropylene and ethylene/propylene copolymers. The gas phase process employed can be, for example, of the type which employs a mechanically stirred bed or a gas fluidized bed as the polymerization reaction zone. Preferred is the process wherein the polymerization reaction is carried out in a vertical cylindrical polymerization reactor containing a fluidized bed of polymer particles supported or suspended above a perforated plate, the fluidization grid, by a flow of fluidization gas.

The gas employed to fluidize the bed comprises the monomer or monomers to be polymerized, and also serves as a heat exchange medium to remove the heat of reaction from the bed. The hot gases emerge from the top of the reactor, normally via a tranquilization zone, also known as a velocity reduction zone, having a wider diameter than the fluidized bed and wherein fine particles entrained in the gas stream have an opportunity to gravitate back into the bed. It can also be advantageous to use a cyclone to remove ultra-fine particles from the hot gas stream. The gas is then normally recycled to the bed by means of a blower or compressor and one or more heat exchangers to strip the gas of the heat of polymerization.

A preferred method of cooling of the bed, in addition to the cooling provided by the cooled recycle gas, is to feed a volatile liquid to the bed to provide an evaporative cooling effect,

often referred to as operation in the condensing mode. The volatile liquid employed in this case can be, for example, a volatile inert liquid, for example, a saturated hydrocarbon having 3 to 8, preferably 4 to 6, carbon atoms. In the case that the monomer or comonomer itself is a volatile liquid, or can be condensed to provide such a liquid, this can suitably be fed to the bed to provide an evaporative cooling effect. The volatile liquid evaporates in the hot fluidized bed to form gas which mixes with the fluidizing gas. If the volatile liquid is a monomer or comonomer, it will undergo some polymerization in the bed. The evaporated liquid then emerges from the reactor as part of the hot recycle gas, and enters the compression/heat exchange part of the recycle loop. The recycle gas is cooled in the heat exchanger and, if the temperature to which the gas is cooled is below the dew point, liquid will precipitate from the gas. This liquid is desirably recycled continuously to the fluidized bed. It is possible to recycle the precipitated liquid to the bed as liquid droplets carried in the recycle gas stream. This type of process is described, for example in EP-89691; U.S. 4,543,399; WO-94/25495 and U.S. 5,352,749. A particularly preferred method of recycling the liquid to the bed is to separate the liquid from the recycle gas stream and to reinject this liquid directly into the bed, preferably using a method which generates fine droplets of the liquid within the bed. This type of process is described in WO-94/28032.

The polymerization reaction occurring in the gas fluidized bed is catalyzed by the continuous or semi-continuous addition of catalyst. Such catalyst can be supported on an inorganic or organic support material as described above. The catalyst can also be subjected to a prepolymerization step, for example, by polymerizing a small quantity of olefin monomer in a liquid inert diluent, to provide a catalyst composite comprising catalyst particles embedded in olefin polymer particles.

The polymer is produced directly in the fluidized bed by catalyzed copolymerization of the monomer and one or more comonomers on the fluidized particles of catalyst, supported catalyst or prepolymer within the bed. Start-up of the polymerization reaction is achieved using a bed of preformed polymer particles, which are preferably similar to the target polyolefin, and conditioning the bed by drying with inert gas or nitrogen prior to introducing the catalyst, the monomers and any other gases which it is desired to have in the recycle gas stream, such as a diluent gas, hydrogen chain transfer agent, or an inert condensable gas when operating in gas phase condensing mode. The produced polymer is discharged continuously or discontinuously from the fluidized bed as desired.

The gas phase processes most suitable for the practice of this invention are continuous processes which provide for the continuous supply of reactants to the reaction zone of the reactor and the removal of products from the reaction zone of the reactor, thereby providing a steady-

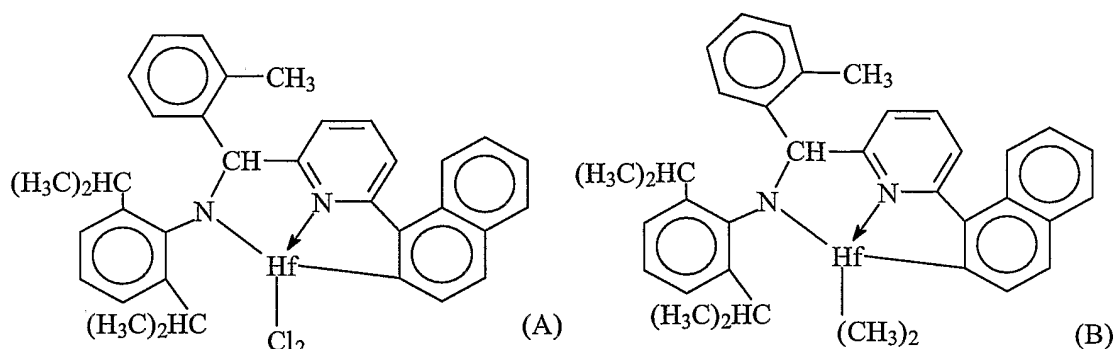
state environment on the macro scale in the reaction zone of the reactor. Products are readily recovered by exposure to reduced pressure and optionally elevated temperatures (devolatilization) according to known techniques. Typically, the fluidized bed of the gas phase process is operated at temperatures greater than 50°C, preferably from 60°C to 110°C, more preferably from 70°C to 110°C.

A number of patents and patent applications describe gas phase processes which are adaptable for use in the process of this invention, particularly, U.S. Patents 4,588,790; 4,543,399; 5,352,749; 5,436,304; 5,405,922; 5,462,999; 5,461,123; 5,453,471; 5,032,562; 5,028,670; 5,473,028; 5,106,804; 5,556,238; 5,541,270; 5,608,019; 5,616,661; and EP applications 659,773; 692,500; 780,404; 697,420; 628,343; 593,083; 676,421; 683,176; 699,212; 699,213; 721,798; 728,150; 728,151; 728,771; 728,772; 735,058; and PCT Applications WO-94/29032, WO-94/25497, WO-94/25495, WO-94/28032, WO-95/13305, WO-94/26793, WO-95/07942, WO-97/25355, WO-93/11171, WO-95/13305, and WO-95/13306.

The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed.

The following examples are provided as further illustration of the invention and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis. The term "overnight", if used, refers to a time of approximately 16-18 hours, the term "room temperature", refers to a temperature of 20-25 °C, and the term "mixed alkanes" refers to a mixture of C₆₋₉ aliphatic hydrocarbons available under the trade designation Isopar E[®], from Exxon Chemicals Inc. In the event the name of a compound herein does not conform to the structural representation thereof, the structural representation shall control. The synthesis of all metal complexes and the preparation of all screening experiments were carried out in a dry nitrogen atmosphere using dry box techniques. All solvents used were HPLC grade and were dried before use.

Examples

Example 1Hafnium Complex Preparation

To a 50 mL flask equipped with a stirrer in a glovebox at room temperature was added 20
 5 ml of toluene and 483 mg (1.00 mmol) of (2,6-di(1-methylethyl)phenylamino)(o-tolyl)((α -
 naphthalenyl(6-pyridin-2-diyl)methane). Two equivalents of isobutyllithium were added
 followed by one equivalent of hafnium tetrachloride. The product, [N-(2,6-di(1-
 methylethyl)phenylamido)(o-tolyl)((α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium
 dichloride (A) was recovered by filtration and subjected to drying under dynamic vacuum. The
 10 dimethyl derivative, [N-(2,6-di(1-methylethyl)phenylamido)(o-tolyl)((α -naphthalen-2-diyl(6-
 pyridin-2-diyl)methane)]hafnium dimethyl (B), was prepared by contacting a toluene solution of
 the dichloride complex with two equivalents of methyl lithium, filtering, removing the volatiles
 and recrystallizing from hexane.

Polymerization

15 A 2 liter stirred, jacketed, polymerization reactor was charged with 400 g mixed alkanes
 solvent and 93 g propylene. Next, 1.5 μ mole of catalyst (B) and 1.8 μ mole cocatalyst
 (methyl di(octadecylammonium) tetrakis(pentafluorophenyl)borate) as 0.005 M solutions in
 toluene, along with isopropylaluminum modified methylalumoxane (PMAO-IP, available from
 Akzo, Inc., 45 μ mol, based on Al, added as a scavenger) were premixed and added via a transfer
 20 line which was subsequently washed three times with 5 ml toluene. Hydrogen was added as a
 molecular weight control agent by differential pressure expansion from a 75 ml addition tank at
 25 psi (345 kPa). In run 1, ethylene (5.3 g) was added. The reactor was heated to the
 polymerization temperature of 100 °C. After 21 minutes polymerization time, the resulting
 polymer solution was removed from the reactor into a nitrogen purged collection vessel
 25 containing 100 ml of isopropyl alcohol and 20 ml of a toluene solution containing 6.7 mg
 hindered phenol antioxidant (Irganox™ 1010 available from Ciba Geigy Co.) and 13.4 mg of
 phosphorus stabilizer (Irgafos™ 168, available from Ciba Geigy Co.). The polymer solution was

then dried in a vacuum oven under gradually increasing temperature and gradually decreasing pressure. The polymer was held at a final temperature of 140° C and a final pressure of 100 torr (13 kPa). Total drying time was 20 hours. Results are contained in Table 1.

Table 1

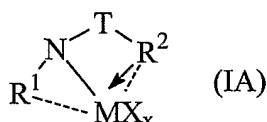
run	yield (g)	efficiency (g/μg Hf)	Mp	Mw	Mn	Mw/Mn
1	63.4	0.237	136.7	639,000	198,000	3.2
2*	35.6	0.133	147.1	387,000	130,000	3.0

5

* comparative not an example of the invention

CLAIMS:

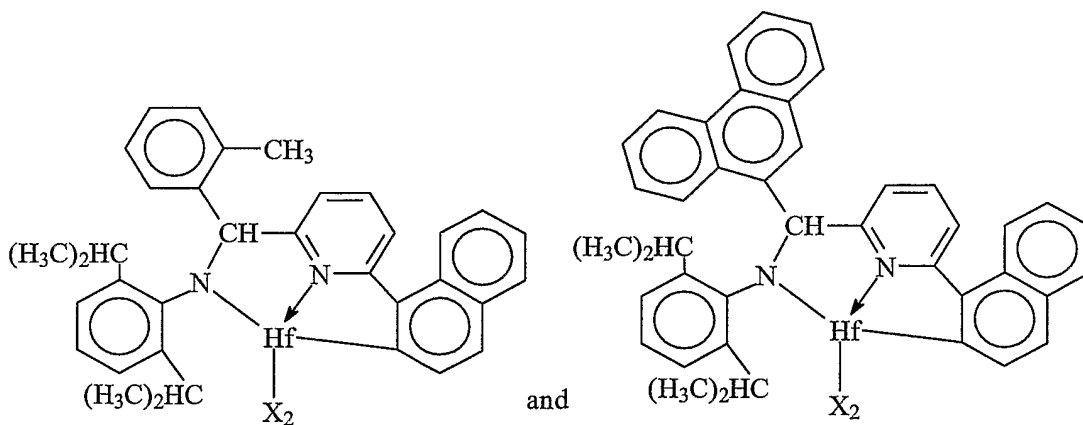
1. A process for preparing interpolymers of ethylene and one or more C₃₋₈ olefin monomers comprising contacting a monomer mixture comprising ethylene and one or more C₃₋₈ olefin monomers with a catalyst composition comprising a Group 4 metal complex of a polyvalent, Lewis base ligand under addition polymerization conditions.
2. A process according to claim 1 wherein the metal complex corresponds to the formula:



wherein

- 10 R¹ is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen;
- T is a divalent bridging group of from 1 to 20 atoms other than hydrogen, preferably a mono- or di- C₁₋₂₀ hydrocarbyl substituted methylene or silane group, and
- 15 R² is a C₆₋₂₀ heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group,
- M is the Group 4 metal, preferably hafnium,
- X is an anionic, neutral or dianionic ligand group,
- x is a number from 0 to 5 indicating the number of such X groups, and
- 20 bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

3. A process according to claim 2 wherein the metal complex is selected from the group consisting of:



wherein X each occurrence is halide, N,N-dimethylamido, or C₁₋₄ alkyl.

4. A process according to claim 1 wherein a mixture comprising propylene and from 0.1 to 10 weight percent ethylene is copolymerized.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/28873

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F210/06 C08F4/642

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)
IPC 7 C08F

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

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

CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02 38628 A (SYMYX TECHNOLOGIES INC) 16 May 2002 (2002-05-16) cited in the application page 86 -page 91; tables 5,6 page 98; example 11 page 112; example 16 page 73 -page 75 claims 54,82-84,88-90 ----- -/---	1-4

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *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 when the document is taken alone
- *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

Date of the actual completion of the international search

23 January 2004

Date of mailing of the international search report

09/02/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Parry, J

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 03/28873

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SUGIMURA, KENJI ET AL: "Olefin polymerization catalysts for producing polyolefins with narrow molecular weight distribution" retrieved from STN Database accession no. 134:116329 XPO02267944 abstract & JP 2001 011111 A (MITSUI CHEMICAL INDUSTRY CO., LTD., JAPAN) 16 January 2001 (2001-01-16) example 3 ---	1-4
X	US 6 103 657 A (MURRAY REX EUGENE) 15 August 2000 (2000-08-15) cited in the application example 5C; table 2 ---	1-4
P,X	WO 03 040201 A (DOW CHEMICAL CO ;STEVENS JAMES C (US); VANDERLENDE DANIEL D (US)) 15 May 2003 (2003-05-15) page 91 -page 98; examples CATG,CATH,,2,6; tables 2-6 page 118 -page 121; tables 18,19 ---	1-4
P,X	WO 03 040202 A (DOW GLOBAL TECHNOLOGIES INC ;BOSNYAK CLIVE (US); KARANDE SEEMA (US) 15 May 2003 (2003-05-15) figures 12G,1H,12J,2-6 page 67 -page 78; examples CATG,CATH,2-6; tables 2-7,10 ---	1-4
P,X	WO 03 040195 A (DOW GLOBAL TECHNOLOGIES INC ;PAINTER ROGER B (US); VOSEPKA PAUL C) 15 May 2003 (2003-05-15) claim 6; table 1 -----	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 03/28873

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0238628	A	16-05-2002	AU 2566202 A	21-05-2002
			AU 4151702 A	18-06-2002
			EP 1334139 A2	13-08-2003
			EP 1364974 A2	26-11-2003
			WO 0238628 A2	16-05-2002
			WO 0246249 A2	13-06-2002
			US 2002173419 A1	21-11-2002
			US 2002147288 A1	10-10-2002
			US 2002142912 A1	03-10-2002
			US 2002137845 A1	26-09-2002
			US 2002156279 A1	24-10-2002
			US 2002177711 A1	28-11-2002
			JP 2001011111	A
US 6103657	A	15-08-2000	US 2002065379 A1	30-05-2002
			US 6320005 B1	20-11-2001
			AT 237622 T	15-05-2003
			AU 735915 B2	19-07-2001
			AU 8380698 A	25-01-1999
			BR 9810213 A	02-10-2001
			DE 69813556 D1	22-05-2003
			EP 0993464 A1	19-04-2000
			ES 2191946 T3	16-09-2003
			JP 2001524162 T	27-11-2001
			TW 467921 B	11-12-2001
			WO 9901460 A1	14-01-1999
			US 6320002 B1	20-11-2001
			US 6265513 B1	24-07-2001
			US 2001034297 A1	25-10-2001
ZA 9805782 A	21-01-1999			
WO 03040201	A	15-05-2003	WO 03040201 A1	15-05-2003
			WO 03040202 A2	15-05-2003
			WO 03040195 A1	15-05-2003
			WO 03040233 A2	15-05-2003
			WO 03040095 A2	15-05-2003
			WO 03040442 A1	15-05-2003
			US 2003204017 A1	30-10-2003
			US 2003195299 A1	16-10-2003
			US 2003176611 A1	18-09-2003
			US 2003195300 A1	16-10-2003
			US 2003194575 A1	16-10-2003
WO 03040202	A	15-05-2003	US 2003204017 A1	30-10-2003
			WO 03040201 A1	15-05-2003
			WO 03040202 A2	15-05-2003
			WO 03040195 A1	15-05-2003
			WO 03040233 A2	15-05-2003
			WO 03040095 A2	15-05-2003
			WO 03040442 A1	15-05-2003
			US 2003195299 A1	16-10-2003
			US 2003176611 A1	18-09-2003
			US 2003195300 A1	16-10-2003
			US 2003194575 A1	16-10-2003
WO 03040195	A	15-05-2003	US 2003204017 A1	30-10-2003
			WO 03040201 A1	15-05-2003

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 03/28873

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03040195	A	WO 03040202 A2	15-05-2003
		WO 03040195 A1	15-05-2003
		WO 03040233 A2	15-05-2003
		WO 03040095 A2	15-05-2003
		WO 03040442 A1	15-05-2003
		US 2003195299 A1	16-10-2003
		US 2003176611 A1	18-09-2003
		US 2003195300 A1	16-10-2003
		US 2003194575 A1	16-10-2003
