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Canadian Intellectual Property Office
An agency of Industry Canada

CA 2742454 A1 2012/12/09

(21) 2 742 454

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 2011/06/09

(41) Mise à la disp. pub./Open to Public Insp.: 2012/12/09

(51) Cl.Int./Int.Cl. *C08F 4/649* (2006.01),
C08F 2/34 (2006.01), *C08F 210/16* (2006.01),
C08F 4/02 (2006.01), *C08F 4/6592* (2006.01)

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(54) Titre : METHODES DE REGULATION DES PROPRIETES DE COPOLYMERE ETHYLENIQUE
(54) Title: METHODS FOR CONTROLLING ETHYLENE COPOLYMER PROPERTIES

(57) Abrégé/Abstract:
A method for altering the polymer architecture of ethylene copolymers made with a supported phosphinimine polymerization catalyst. The method involves changing the amount of a catalyst modifier added to a reactor separately from or together with a supported phosphinimine polymerization catalyst.

METHODS FOR CONTROLLING ETHYLENE COPOLYMER PROPERTIES

ABSTRACT OF THE DISCLOSURE

A method for altering the polymer architecture of ethylene copolymers made with a supported phosphinimine polymerization catalyst. The method involves changing the amount of a catalyst modifier added to a reactor separately from or together with a supported phosphinimine polymerization catalyst.

METHODS FOR CONTROLLING ETHYLENE COPOLYMER PROPERTIES

FIELD OF THE INVENTION

The present invention relates to supported phosphinimine catalysts, which when treated directly or indirectly with different amounts of a catalyst modifier, give rise to different ethylene copolymer architectures during gas phase polymerization, allowing for polymer architecture manipulation.

BACKGROUND OF THE INVENTION

Gas phase olefin polymerization with single site catalysts has been a well established art field since the invention of metallocene catalysts over two decades ago. Although, single site polymerization catalysts (such as metallocene catalysts, constrained geometry catalysts, and phosphinimine catalysts) are often chosen for their very high activity, the use of such catalysts can lead to reactor fouling especially in a fluidized bed gas phase reactor. Such fouling may include polymer agglomeration, sheeting, or chunking, and may ultimately require reactor shut down.

In order to improve reactor operability, several specialized catalyst preparative methods, operating conditions, and additives have been used to modify the performance of metallocenes and to reduce reactor fouling.

European Pat. Appl. No. 630,910 discusses reversibly reducing the activity of a metallocene catalyst using a Lewis base compound such as for example an amine compound.

Long chain substituted alkanolamine compounds in particular, have been used in combination with metallocenes to reduce the amount of reactor fouling in fluidized bed polymerization processes. The use of substituted alkanolamines in combination with metallocene catalysts to improve reactor operability and reduce static levels is described in European Pat. Appl. No. 811,638 and in U.S. Pat. Nos

5,712,352; 6,201,076; 6,476,165; 6,180,729; 6,977,283; 6,114,479; 6,140,432; 6,124,230; 6,117,955; 5,763,543; and 6,180,736. Alkanolamines have been added to a metallocene catalyst prior to addition to a reaction zone, as described in U.S. Pat. Nos 6,140,432; 6,124,230 and 6,114,479. Alkanolamines have also been added directly to a reactor or other associated parts of a fluidized bed reactor processes such as the recycle stream loop as is taught in European Pat. Appl. No. 811,638 and in U.S. Pat. No. 6,180,729 respectively.

There has been no systematic exploration of the affect of long chain substituted amines, including monoalkanolamines and dialkanolamines, on supported phosphinimine catalysts.

SUMMARY OF THE INVENTION

The inventors have now discovered that, surprisingly, direct or indirect treatment of a supported phosphinimine catalyst with different amounts of a suitable catalyst modifier, allows one to alter and hence control to some extent the architecture of an ethylene copolymer made using such a catalyst. The change in the ethylene copolymer architecture is manifested by a change in the composition distribution of the ethylene copolymer. Indices which characterize changes in composition distribution include changes to one or more of the following: A) the composition distribution breadth index (CDBI) of the ethylene copolymer as measured using temperature rising elution fractionation (TREF) methods; B) the weight percent of a higher temperature eluting material (i.e. from 90°C to 105°C) observed in a TREF profile obtained for the ethylene copolymer; and C) the comonomer distribution vs. molecular weight (i.e. the comonomer distribution profile) in the ethylene copolymer as measured by gel permeation chromatography with Fourier transform Infra-red detection (GPC-FTIR).

To alter the composition distribution of an ethylene copolymer, the amount of catalyst modifier fed to a polymerization reactor is changed, the amount of catalyst modifier included in a polymerization catalyst is changed prior to feeding the polymerization catalyst to a reactor, or both.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain amine compound represented by the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1.

In an embodiment of the invention, the olefin polymerization catalyst comprises: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, the olefin polymerization catalyst comprises: a phosphinimine catalyst, an inert support, a cocatalyst; and further includes a catalyst modifier.

Accordingly, provided is a method for altering the composition distribution of an ethylene copolymer, the method comprising:

introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising a phosphinimine catalyst, an inert support, and a cocatalyst;

feeding from 0 to 100 ppm of a catalyst modifier into the reactor (based on the weight of copolymer produced), the catalyst modifier comprising a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and

polymerizing ethylene and an alpha-olefin in the reactor to give the ethylene copolymer;

wherein the composition distribution of the ethylene copolymer is altered by changing the amount of the catalyst modifier fed to the reactor by at least 5 ppm (based on the weight of copolymer produced).

Also provided is a method for altering the composition distribution of an ethylene copolymer, the method comprising:

introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 weight percent of a catalyst modifier based on the weight of i), ii) and iii) of the polymerization catalyst, the catalyst modifier comprising a compound having the formula $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and

polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer;

wherein the composition distribution of the ethylene copolymer is altered by changing the amount of the catalyst modifier included in the olefin polymerization catalyst by at least 0.25 weight percent.

Also provided is a method for altering the composition distribution of an ethylene copolymer, the method comprising:

introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst

and further including from 0 to 10 wt% of a catalyst modifier (based on the weight of i), ii) and iii) of the polymerization catalyst); feeding from 0 to 100 ppm of a catalyst modifier into the gas phase reactor (based on the weight of the copolymer produced); and

polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer;

wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor comprises a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and

wherein the composition distribution of the ethylene copolymer is altered by changing at least one of the following:

a) the amount of the catalyst modifier fed into the gas phase reactor by at least 5 ppm (based on the weight of copolymer produced);

b) the amount the catalyst modifier included in the polymerization catalyst by at least 0.5 wt% (based on the weight of i), ii) and iii) of the polymerization catalyst).

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula: $R^1N((CH_2)_nOH)((CH_2)_mOH)$ where R^1 is a hydrocarbyl group having anywhere from 5 to 30 carbon atoms, and n and m are integers from 1-20.

In an embodiment of the invention, the catalyst modifier comprises at least one compound represented by the formula: $R^1N((CH_2)_xOH)_2$ where R^1 is a hydrocarbyl group having anywhere from 6 to 30 carbon atoms, and x is 2 or 3.

In an embodiment of the invention, the catalyst modifier comprises at least one compound represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a hydrocarbyl group having anywhere from 8 to 22 carbon atoms.

In an embodiment of the invention, the phosphinimine catalyst has the formula: $(L)(PI)MX_2$, where M is Ti, Zr or Hf; PI is a phosphinimine ligand having the formula $R_3P=N-$, where R is independently selected from the group consisting of hydrogen, halogen, and C_1-C_{20} hydrocarbyl; L is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl, and substituted fluorenyl; and X is an activatable ligand.

Brief Description of the Drawings

Figure 1 shows the GPC-FTIR for a copolymer made during a baseline run (poly. Run. No. 6).

Figure 2 shows the TREF profile for a copolymer made during a baseline run (poly. Run. No. 6).

Figure 3 shows the GPC-FTIR for a copolymer made with a catalyst comprising 1.5 wt% of Amter-163 (poly. Run. No. 2).

Figure 4 shows the TREF profile for a copolymer made with a catalyst comprising 1.5 wt% of Amter-163 (poly. Run. No. 2).

Figure 5 shows the GPC-FTIR for a copolymer made with a catalyst comprising 1.5 wt% of Armostat-1800 (poly. Run. No. 4).

Figure 6 shows the TREF profile for a copolymer made with a catalyst comprising 1.5 wt% of Amter-163 (poly. Run. No. 4).

Figure 7 shows the GPC-FTIR for a copolymer made with a catalyst comprising 2.5 wt% of Armostat-1800 (poly. Run. No. 9).

Figure 8 shows the GPC-FTIR for a copolymer made with a catalyst comprising 3.5 wt% of Armostat-1800 (poly. Run. No. 11).

Figure 9 shows the GPC-FTIR for a copolymer made when 25 ppm of Atmer-163 is fed directly to the polymerization reactor (poly. Run. No.14).

Figure 10 shows the TREF profile for a copolymer made when 25 ppm of Atmer-163 is fed directly to the polymerization reactor (poly. Run. No.14).

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In the present invention, a "catalyst modifier" which, when combined with a phosphinimine based polymerization catalyst in various amounts, alters the architecture of ethylene copolymer products obtained in a polymerization process. The catalyst modifier can be combined with a polymerization catalyst comprising a phosphinimine catalyst, an inert support and a cocatalyst, by adding it directly to the polymerization reactor, making it part of the polymerization catalyst formulation, or both. The change in the ethylene copolymer architecture is manifested by a change in the "composition distribution" of the ethylene copolymer. Indices which when changed characterize changes in the composition distribution of the ethylene copolymer include one or more of the following:

A) the composition distribution breadth index (CDBI) of the ethylene copolymer as measured using temperature rising elution fractionation (TREF) methods;

B) the weight percent of a higher temperature eluting material (i.e. from 90°C to 105°C) observed in TREF profile obtained for the ethylene copolymer; and

C) the comonomer distribution relative to molecular weight in the ethylene copolymer as measured by gel permeation chromatography with Fourier transform infra-red detection (GPC-FTIR).

The Catalyst Modifier

The catalyst modifier employed in the present invention comprises a long chain amine compound. In the present invention, the terms "long chain substituted amine" or "long chain amine" are defined as tri-coordinate nitrogen compounds (i.e. amine based compounds) containing at least one hydrocarbyl group having at least 5 carbon atoms, preferably from 6 to 30 carbon atoms. The terms "hydrocarbyl" or "hydrocarbyl group" includes branched or straight chain hydrocarbyl groups which may be fully saturated groups (i.e. have no double or triple bonding moieties) or which may be partially unsaturated (i.e. they may have one or more double or triple bonding moieties). The long chain hydrocarbyl group may also contain un-saturation in the form of aromatic ring moieties attached to or part of the main chain. Preferably, the long chain amine (i.e. the tri-coordinate nitrogen compound) will also have at least one heteroatom containing hydrocarbyl group. Such heteroatom containing hydrocarbyl groups can be branched or straight chain hydrocarbyl groups or substituted hydrocarbyl groups having one or more carbon atoms and at least one heteroatom. Heteroatom containing hydrocarbyl groups may also contain unsaturated moieties. Suitable heteroatoms include for example, oxygen, nitrogen, phosphorus or sulfur. Other groups which may be attached to nitrogen in a long chain substituted amine compound are generally selected from hydrocarbyl groups having one or more carbon atoms and/or a hydrogen group (H).

In embodiments of the invention, the long chain amine is a long chain substituted monoalkanolamine, or a long chain substituted dialkanolamine. These amines have one or two alcoholhydrocarbyl groups respectively as well as a hydrocarbyl group having at least 5 carbons.

In an embodiment of the invention, the catalyst modifier employed comprises at least one long chain amine compound represented by the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted monoalkanolamine represented by the formula $R^1R^2N((CH_2)_nOH)$ where R^1 is a hydrocarbyl group having anywhere from 5 to 30 carbon atoms, R^2 is a hydrogen or a hydrocarbyl group having anywhere from 1 to 30 carbon atoms, and n is an integer from 1-20.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula: $R^1N((CH_2)_nOH)((CH_2)_mOH)$ where R^1 is a hydrocarbyl group having anywhere from 5 to 30 carbon atoms, and n and m are integers from 1-20.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula: $R^1N((CH_2)_xOH)_2$ where R^1 is a hydrocarbyl group having anywhere from 6 to 30 carbon atoms, and x is an integer from 1-20.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula: $R^1N((CH_2)_xOH)_2$ where R^1 is a hydrocarbyl group having anywhere from 6 to 30 carbon atoms, and x is 2 or 3.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula:

$R^1N((CH_2)_xOH)_2$ where R^1 is a linear hydrocarbyl group having anywhere from 6 to 30 carbon atoms, and x is 2 or 3.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a linear hydrocarbyl group having anywhere from 6 to 30 carbon atoms.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a linear, saturated alkyl group having anywhere from 6 to 30 carbon atoms.

In an embodiment of the invention, the catalyst modifier comprises at least one long chain substituted dialkanolamine represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a hydrocarbyl group having anywhere from 8 to 22 carbon atoms.

In an embodiment of the invention, the catalyst modifier comprises a long chain substituted dialkanolamine represented by the formula: $C_{18}H_{37}N(CH_2CH_2OH)_2$.

In an embodiment of the invention, the catalyst modifier comprises long chain substituted dialkanolamines represented by the formulas: $C_{13}H_{27}N(CH_2CH_2OH)_2$ and $C_{15}H_{31}N(CH_2CH_2OH)_2$.

In an embodiment of the invention, the catalyst modifier comprises a mixture of long chain substituted dialkanolamines represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a hydrocarbyl group having anywhere from 8 to 18 carbon atoms.

Non limiting examples of catalyst modifiers which can be used in the present invention are Kemamine AS-990^{TM}, Kemamine AS-650^{TM}, Armostat-1800^{TM}, bis-hydroxy-cocoamine, 2,2′-octadecyl-amino-bisethanol, and Atmer-163^{TM}.

The long chain substituted amine may also be a polyoxyethylenehydrocarbyl amine.

In an embodiment of the invention, the catalyst modifier comprises a polyoxyethylenehydrocarbyl amine represented by the formula: $R^1N((CH_2CH_2O)_nH)((CH_2CH_2O)_mH)$, where R^1 is a hydrocarbyl group having from 5 to 30 carbons, and n and m are integers from 1-10 or higher (i.e. polymeric).

Addition of the Catalyst Modifier

To alter the composition distribution of an ethylene copolymer made using a polymerization catalyst comprising a phosphinimine catalyst, an inert support and a cocatalyst; a catalyst modifier (defined as above) is added to a reactor zone (or associated process equipment) separately from the polymerization catalyst, as part of the polymerization catalyst, or both.

The amount of catalyst modifier added to a reactor (or other associated process equipment) is conveniently represented herein as the parts per million (ppm) of catalyst modifier based on the weight of copolymer produced.

The amount of catalyst modifier included in a polymerization catalyst is conveniently represented herein as a weight percent (wt%) of the catalyst modifier based on the combined weight of the phosphinimine catalyst, the inert support and the cocatalyst. In order to avoid any ambiguity, the phrase “weight of the polymerization catalyst” includes the weight of the phosphinimine catalyst, the inert support, and the cocatalyst but not the weight of the catalyst modifier.

The catalyst modifier may be added to a polymerization reactor in a number of ways. The catalyst modifier may be added to a reactor system separately from the polymerization catalyst or it may be combined with the polymerization catalyst prior to feeding the combination to a reactor system.

If the catalyst modifier is added to the polymerization catalyst prior to adding the polymerization catalyst to a reactor, then the catalyst modifier can be added at any point during the preparation of the polymerization catalyst. Thus, at least one phosphinimine catalyst, at least one activator, at least one inert support and at least one catalyst modifier may be combined in any order to form a supported catalyst suitable for use in the present invention. In specific embodiments of the invention: the catalyst modifier may be added to a support after both the phosphinimine catalyst and the cocatalyst have been added; the catalyst modifier may be added to a support before either of the phosphinimine catalyst or the cocatalyst are added; the catalyst modifier may be added to a support after the phosphinimine catalyst but before the cocatalyst; the catalyst modifier may be added to a support after the cocatalyst but before the phosphinimine catalyst. Also, the catalyst modifier can be added in portions during any stage of the preparation of the polymerization catalyst.

In an embodiment of the present invention, the catalyst modifier is added to a polymerization catalyst already comprising the phosphinimine catalyst, inert support and cocatalyst. The catalyst modifier can be added to the polymerization catalyst offline and prior to addition of the polymerization catalyst to the polymerization zone, or the catalyst modifier may be added to the polymerization catalyst on route to a polymerization reactor.

The catalyst modifier may be included in the polymerization catalyst (or where appropriate, added to a polymerization catalyst component or components

which comprise at least one of the phosphinimine catalyst, the inert support and the cocatalyst) in any suitable manner. By way of non-limiting example, the catalyst modifier may be dry blended (if it is a solid) with the polymerization catalyst (or a polymerization catalyst component) or it may be added neat (if the catalyst modifier is a liquid) or it may be added as solution or slurry in a suitable hydrocarbon solvent or diluent respectively. The polymerization catalyst (or polymerization catalyst components) can likewise be put into solution or made into a slurry using suitable solvents or diluents respectively, followed by addition of the catalyst modifier (as a neat solid or liquid or as a solution or a slurry in suitable solvents or diluents) or vice versa. Alternatively, the catalyst modifier may be deposited onto a separate support and the resulting supported catalyst modifier blended either dry or in a slurry with the polymerization catalyst (or a polymerization catalyst component).

In an embodiment of the present invention, the catalyst modifier is added to a polymerization catalyst already comprising the phosphinimine catalyst, inert support and cocatalyst. The catalyst modifier can be added to the polymerization catalyst offline and prior to addition of the polymerization catalyst to the polymerization zone, or the catalyst modifier may be added to the polymerization catalyst on route to a reactor.

The catalyst modifier may be fed to a reactor system using any appropriate method known to persons skilled in the art. For example, the catalyst modifier may be fed to a reactor system as a solution or as a slurry in a suitable solvent or diluent respectively. Suitable solvents or diluents are inert hydrocarbons well known to persons skilled in the art and generally include aromatics, paraffins, and cycloparaffinics such as for example benzene, toluene, xylene, cyclohexane, fuel oil, isobutane, mineral oil, kerosene and the like. Further specific examples include but

are not limited to hexane, heptanes, isopentane and mixtures thereof. Alternatively, the catalyst modifier may be added to an inert support material and then fed to a polymerization reactor as a dry feed or a slurry feed. The catalyst modifier may be fed to various locations in a reactor system. When considering a fluidized bed process for example, the catalyst modifier may be fed directly to any area of the reaction zone, or any area of the entrainment zone, or it may be fed to any area within the recycle loop, where such areas are found to be effective sites at which to feed a catalyst modifier.

When added as a solution or mixture with a solvent or diluent respectively, the catalyst modifier may make up, for example, from 0.1 to 30 wt% of the solution or mixture, or from 0.1 to 20 wt%, or from 0.1 to 10 wt%, or from 0.1 to 5 wt% or from 0.1 to 2.5 wt% or from 0.2 to 2.0 wt%, although a person skilled in the art will recognize that further, possibly broader ranges, may also be used and so the invention should not be limited in this regard.

The catalyst modifier can be added to a reactor with all or a portion of one or more of the monomers or the cycle gas.

The catalyst modifier can be added to a reactor through a dedicated feed line or added to any convenient feed stream including an ethylene feed stream, a comonomer feed stream, a catalyst feed line or a recycle line.

The catalyst modifier can be fed to a location in a fluidized bed system in a continuous or intermittent manner.

In an embodiment of the invention, the rate of addition of a catalyst modifier to a reactor will be programmed using measured reactor static levels (or other lead indicators such as reactor temperature) as programming inputs, so as to maintain a

constant or pre-determined level of static (or for example, temperature) in a polymerization reactor.

The catalyst modifier can be added to a reactor at a time before, after or during the start of the polymerization reaction

The catalyst modifier may be added to the polymerization catalyst or to one or more polymerization catalyst components (i.e. phosphinimine catalyst, inert support, or cocatalyst) on route to a reaction zone.

In an embodiment of the invention, the catalyst modifier is added directly to a reaction zone, separately from the polymerization catalyst. Most typically, it is so added by spraying a solution or mixture of the catalyst modifier directly into a reaction zone.

In an embodiment of the invention, the catalyst modifier is combined with the polymerization catalyst before adding the combination directly to a reaction zone.

In an embodiment of the invention, the catalyst modifier is added to a polymer seed bed present in a reactor prior to starting the polymerization reaction by introduction of a catalyst.

In an embodiment of the invention, the catalyst modifier is added directly to a reaction zone, separately from a polymerization catalyst, and the catalyst modifier is added as a mixture with an inert hydrocarbon.

In an embodiment of the invention, the catalyst modifier is added directly to a reaction zone, separately from a polymerization catalyst, and the catalyst modifier is added as a mixture with an inert hydrocarbon, and is added during a polymerization reaction.

The total amount of catalyst modifier that may be fed to a reactor and/or included in the polymerization catalyst is not specifically limited, but it should not

exceed an amount which causes the phosphinimine based polymerization catalyst activity to drop to below that which would be commercially acceptable.

In this regard, the amount of catalyst modifier fed to a reactor will generally not exceed about 150 ppm, or 100 ppm, or 75 ppm, or 50 ppm, or 25 ppm (parts per million based on the weight of the (co)polymer being produced) while the amount of catalyst modifier included in the polymerization catalyst will generally not exceed about 10 weight percent (based on the combined weight of the phosphinimine catalyst, the inert support and the cocatalyst).

In embodiments of the invention, the catalyst modifier fed to a reactor will be from 150 to 0 ppm, and including narrower ranges within this range, such as but not limited to, from 150 to 1 ppm, or from 150 to 5 ppm, or from 100 to 0 ppm, or from 100 to 1 ppm, or from 100 to 5 ppm, or from 75 to 0 ppm, or from 75 to 1 ppm, or from 75 to 5 ppm, or from 50 to 0 ppm, or from 50 to 1 ppm, or from 50 to 5 ppm, or from 25 to 0 ppm, or from 25 to 1 ppm, or from 25 to 5 ppm (parts per million by weight of the polymer being produced).

In embodiments of the invention, the amount of catalyst modifier included in the polymerization catalyst will be from 0 to 10 weight percent, and including narrower ranges within this range, such as but not limited to, from 0 to 6.0 weight percent, or from 0.25 to 6.0 weight percent, or from 0 to 5.0 weight percent, or from 0.25 to 5.0 weight percent, or from 0 to 4.5 weight percent, or from 0.5 to 4.5 weight percent, or from 1.0 to 4.5 weight percent, or from 0.75 to 4.0 weight percent, or from 0 to 4.0 weight percent, or from 0.5 to 4.0 weight percent, or from 1.0 to 4.0 weight per cent, or from 0 to 3.75 weight percent, or from 0.25 to 3.75 weight percent, or from 0.5 to 3.5 weight percent, or from 1.25 to 3.75 weight percent, or from 1.0 to 3.5 weight percent, or from 1.5 to 3.5 weight percent, or from 0.75 to

3.75 weight percent, or from 1.0 to 3.75 weight percent (wt% is the weight percent of the catalyst modifier based on the combined weight of the phosphinimine catalyst, the inert support and the cocatalyst).

The Polymerization Catalyst

In the present invention, the polymerization catalyst minimally includes a phosphinimine catalyst, an inert support and a cocatalyst. In an embodiment of the invention, the olefin polymerization catalyst will also include a catalyst modifier. Hence, the polymerization catalyst includes a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

The Phosphinimine Catalyst

Some non-limiting examples of phosphinimine catalysts can be found in U.S. Pat. Nos. 6,342,463; 6,235,672; 6,372,864; 6,984,695; 6,063,879; 6,777,509 and 6,277,931 all of which are incorporated by reference herein.

Preferably, the phosphinimine catalyst is based on metals from group 4, which includes titanium, hafnium and zirconium. The most preferred phosphinimine catalysts are group 4 metal complexes in their highest oxidation state.

The phosphinimine catalysts described herein, usually require activation by one or more cocatalytic or activator species in order to provide polymer from olefins.

A phosphinimine catalyst is a compound (typically an organometallic compound) based on a group 3, 4 or 5 metal and which is characterized as having at least one phosphinimine ligand. Any compounds/complexes having a phosphinimine ligand and which display catalytic activity for ethylene (co)polymerization may be called “phosphinimine catalysts”.

In an embodiment of the invention, a phosphinimine catalyst is defined by the formula: $(L)_n(PI)_mMX_p$ where M is a transition metal selected from Ti, Hf, Zr; PI is a

phosphinimine ligand; L is a cyclopentadienyl type ligand or a heteroatom ligand; X is an activatable ligand; m is 1 or 2; n is 0 or 1; and p is determined by the valency of the metal M. Preferably m is 1, n is 1 and p is 2.

In an embodiment of the invention, a phosphinimine catalyst is defined by the formula: $(L)(PI)MX_2$ where M is a transition metal selected from Ti, Hf, Zr; PI is a phosphinimine ligand; L is a cyclopentadienyl type ligand; and X is an activatable ligand.

The phosphinimine ligand is defined by the formula: $R_3P=N-$, where N bonds to the metal, and wherein each R is independently selected from the group consisting of a hydrogen atom; a halogen atom; C_{1-20} hydrocarbyl radicals which are unsubstituted or further substituted by one or more halogen atom and/or C_{1-20} alkyl radical; C_{1-8} alkoxy radical; C_{6-10} aryl or aryloxy radical (the aryl or aryloxy radical optionally being unsubstituted or further substituted by one or more halogen atom and/or C_{1-20} alkyl radical); amido radical; silyl radical of the formula: $-SiR'_3$ wherein each R′ is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals; and germanyl radical of the formula: $-GeR'_3$ wherein R′ is as defined above.

In an embodiment of the invention the phosphinimine ligand is chosen so that each R is a hydrocarbyl radical. In a particular embodiment of the invention, the phosphinimine ligand is tri-(tertiarybutyl)phosphinimine (i.e. where each R is a tertiary butyl group).

In an embodiment of the invention, the phosphinimine catalyst is a group 4 compound/complex which contains one phosphinimine ligand (as described above) and one ligand L which is either a cyclopentadienyl-type ligand or a heteroatom ligand.

As used herein, the term cyclopentadienyl-type ligand is meant to convey its conventional meaning, namely a ligand having a five carbon ring which is bonded to the metal via eta-5 bonding. Thus, the term "cyclopentadienyl-type" includes, for example, unsubstituted cyclopentadienyl, singly or multiply substituted cyclopentadienyl, unsubstituted indenyl, singly or multiply substituted indenyl, unsubstituted fluorenyl and singly or multiply substituted fluorenyl. An exemplary list of substituents for a cyclopentadienyl, indenyl or fluorenyl ligand includes the group consisting of C_{1-10} hydrocarbyl radical (which hydrocarbyl substituents are unsubstituted or further substituted by for example a halide and/or a hydrocarbyl group); a halogen atom; C_{1-8} alkoxy radical; a C_{1-10} aryl or aryloxy radical (each of which may be further substituted by for example a halide and/or a hydrocarbyl group; for example a suitable substituted C_{1-10} group is a perfluoroaryl group such as $-C_6F_5$); an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; silyl radicals of the formula $-Si(R')_3$ wherein each R′ is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals; and germanyl radicals of the formula $-Ge(R')_3$ wherein R′ is as defined directly above.

As used herein, the term "heteroatom ligand" refers to a ligand which contains at least one heteroatom selected from the group consisting of boron, nitrogen, oxygen, silicon, phosphorus or sulfur. The heteroatom ligand may be sigma or pi-bonded to the metal. Exemplary heteroatom ligands include but are not limited to “silicon containing” ligands, “amido” ligands, “alkoxy” ligands, “boron heterocycle” ligands and “phosphole” ligands.

Silicon containing ligands are defined by the formula: -(μ)$SiR^xR^yR^z$ where the "-" denotes a bond to the transition metal and μ is sulfur or oxygen. The substituents on the Si atom, namely R^x, R^y and R^z are required in order to satisfy the bonding orbital of the Si atom. The use of any particular substituent R^x, R^y or R^z is not especially important. In an embodiment of the invention, each of R^x, R^y and R^z is a C_{1-2} hydrocarbyl group (i.e. methyl or ethyl) simply because such materials are readily synthesized from commercially available materials.

The term "amido" is meant to convey its broad, conventional meaning. Thus, these ligands are characterized by (a) a metal-nitrogen bond and (b) the presence of two substituents (which are typically simple alkyl or silyl groups) on the nitrogen atom.

The term "alkoxy" is also intended to convey its conventional meaning. Thus, these ligands are characterized by (a) a metal oxygen bond, and (b) the presence of a hydrocarbyl group bonded to the oxygen atom. The hydrocarbyl group may be a ring structure and may optionally be substituted (e.g. 2,6 di-tertiary butyl phenoxy).

The "boron heterocyclic" ligands are characterized by the presence of a boron atom in a closed ring ligand. This definition includes heterocyclic ligands which also contain a nitrogen atom in the ring. These ligands are well known to those skilled in the art of olefin polymerization and are fully described in the literature (see, for example, U.S. Pat. Nos. 5,637,659 and 5,554,775 and the references cited therein).

The term "phosphole" is also meant to convey its conventional meaning. "Phospholes" are cyclic dienyl structures having four carbon atoms and one phosphorus atom in the closed ring. The simplest phosphole is C_4PH_4 (which is analogous to cyclopentadiene with one carbon in the ring being replaced by

phosphorus). The phosphole ligands may be substituted with, for example, C_{1-20} hydrocarbyl radicals (which may, optionally, contain halogen substituents); phosphido radicals; amido radicals; silyl or alkoxy radicals. Phosphole ligands are also well known to those skilled in the art of olefin polymerization and are described as such in U.S. Pat. No. 5,434,116.

The term "activatable ligand" refers to a ligand which may be activated by a cocatalyst (also referred to as an "activator"), to facilitate olefin polymerization. Examples of activatable ligands X, are independently selected from the group consisting of a hydrogen atom; a halogen atom; a C_{1-10} hydrocarbyl radical; a C_{1-10} alkoxy radical; a C_{5-10} aryl oxide radical, each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; and a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals. Two activatable X ligands may also be joined to one another and form for example, a substituted or unsubstituted diene ligand (i.e. 1,3-diene); or a delocalized heteroatom containing group such as an acetate group.

The number of activatable ligands depends upon the valency of the metal and the valency of the activatable ligand. The preferred phosphinimine catalysts are based on group 4 metals in their highest oxidation state (i.e. 4^+). Particularly suitable activatable ligands are monoanionic such as a halide (e.g. chloride) or a hydrocarbyl (e.g. methyl, benzyl).

In some instances, the metal of the phosphinimine catalyst may not be in the highest oxidation state. For example, a titanium (III) component would contain only one activatable ligand.

In an embodiment of the invention, the phosphinimine catalyst has the formula, $(L)(PI)MX_2$, where M is Ti, Zr or Hf; PI is a phosphinimine ligand having the formula $R_3P=N-$, where R is independently selected from the group consisting of hydrogen, halogen, and C_1-C_{20} hydrocarbyl; L is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl, and substituted fluorenyl; and X is an activatable ligand.

In an embodiment of the invention, the phosphinimine catalyst contains a phosphinimine ligand, a cyclopentadienyl ligand and two chloride or two methyl ligands bonded to the group 4 metal.

In an embodiment of the invention, the phosphinimine catalyst contains a phosphinimine ligand, a substituted cyclopentadienyl ligand and two chloride or two methyl ligands bonded to the group 4 metal.

In an embodiment of the invention, the phosphinimine catalyst contains a phosphinimine ligand, a perfluoroaryl substituted cyclopentadienyl ligand and two chloride or two methyl ligands bonded to the group 4 metal.

In an embodiment of the invention, the phosphinimine catalyst contains a phosphinimine ligand, a perfluorophenyl substituted cyclopentadienyl ligand (i.e. Cp-C_6F_5) and two chloride or two methyl ligands bonded to the group 4 metal.

In an embodiment of the invention, the phosphinimine catalyst contains a 1,2-substituted cyclopentadienyl ligand and a phosphinimine ligand which is substituted by three tertiary butyl substituents.

In an embodiment of the invention, the phosphinimine catalyst contains a 1,2 substituted cyclopentadienyl ligand (e.g. a 1,2-(R^*)(Ar-F)Cp) where the substituents are selected from R^* a hydrocarbyl group, and Ar-F a perfluorinated aryl group, a 2,6

(i.e. ortho) fluoro substituted phenyl group, or a 2,3,5,6 (i.e. ortho/meta) fluoro substituted phenyl group respectively.

In the present invention, 1,2 substituted cyclopentadienyl ligands such as for example 1,2-(R^*)(Ar-F)Cp ligands may contain as impurities 1,3 substituted analogues such as for example 1,3-(R^*)(Ar-F)Cp ligands. Hence, phosphinimine catalysts having a 1,2 substituted Cp ligand may contain as an impurity, a phosphinimine catalyst having a 1,3 substituted Cp ligand. Alternatively, the current invention contemplates the use of 1,3 substituted Cp ligands as well as the use of mixtures of varying amounts of 1,2 and 1,3 substituted Cp ligands to give phosphinimine catalysts having 1,3 substituted Cp ligands or mixed phosphinimine catalysts having 1,2 and 1,3 substituted Cp ligands.

In an embodiment of the invention, the phosphinimine catalyst has the formula: (1,2-(R^*)(Ar-F)Cp)M(N=P(t-Bu)$_3$)X_2 where R^* is a hydrocarbyl group; Ar-F is a perfluorinated aryl group, a 2,6 (i.e. ortho) fluoro substituted phenyl group or a 2,3,5,6 (i.e. ortho/meta) fluoro substituted phenyl group; M is Ti, Zr or Hf; and X is an activatable ligand. In an embodiment of the invention, the phosphinimine catalyst has the formula: (1,2-(R^*)(Ar-F)Cp)M(N=P(t-Bu)$_3$)X_2 where R^* is an alkyl group; Ar-F is a perfluorinated aryl group, a 2,6 (i.e. ortho) fluoro substituted phenyl group or a 2,3,5,6 (i.e. ortho/meta) fluoro substituted phenyl group; M is Ti, Zr or Hf; and X is an activatable ligand. In an embodiment of the invention, the phosphinimine catalyst has the formula: (1,2-(R^*)(Ar-F)Cp)M(N=P(t-Bu)$_3$)X_2 where R^* is a hydrocarbyl group having from 1 to 20 carbons; Ar-F is a perfluorinated aryl group; M is Ti, Zr or Hf; and X is an activatable ligand. In an embodiment of the invention, the phosphinimine catalyst has the formula: (1,2-(n-R^*)(Ar-F)Cp)M(N=P(t-Bu)$_3$)X_2 where R^* is a straight chain alkyl group; Ar-F is a perfluorinated aryl group;

M is Ti, Zr or Hf; and X is an activatable ligand. In an embodiment of the invention, the phosphinimine catalyst has the formula: (1,2-(R^*)(C_6F_5)Cp)M(N=P(t-Bu)$_3$)X_2 where R^* is a hydrocarbyl group having 1 to 20 carbon atoms; M is Ti, Zr or Hf; and X is an activatable ligand. In an embodiment of the invention, the phosphinimine catalyst has the formula: (1,2-(n-R^*)(C_6F_5)Cp)M(N=P(t-Bu)$_3$)X_2 where R^* is a straight chain alkyl group; M is Ti, Zr or Hf; and X is an activatable ligand. In further embodiments, M is Ti and R^* is selected from the group consisting of n-propyl, n-butyl and n-hexyl, and X is selected from chloride or methide.

The term "perfluorinated aryl group" means that each hydrogen atom attached to a carbon atom in an aryl group has been replaced with a fluorine atom as is well understood in the art (e.g. a perfluorinated phenyl group or substituent has the formula $-C_6F_5$). In embodiments of the invention, Ar-F is selected from the group comprising perfluorinated phenyl or perfluorinated naphthyl groups.

Some phosphinimine catalysts which may be used in the present invention include: (1,2-(n-propyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl_2, (1,2-(n-butyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl_2 and (1,2-(n-hexyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl_2.

The Cocatalyst

In the present invention, the phosphinimine catalyst is used in combination with at least one activator (or "cocatalyst") to form an active polymerization catalyst system for olefin polymerization. Activators (i.e. cocatalysts) include ionic activator cocatalysts and hydrocarbyl aluminoxane cocatalysts.

The activator used to activate the phosphinimine catalyst can be any suitable activator including one or more activators selected from the group consisting of alkylaluminoxanes and ionic activators, optionally together with an alkylating agent.

The alkylaluminoxanes are complex aluminum compounds of the formula:

$R^3_2Al^1O(R^3Al^1O)_mAl^1R^3_2$, wherein each R^3 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 3 to 50. Optionally a hindered phenol can be added to the alkylaluminoxane to provide a molar ratio of Al^1:hindered phenol of from 2:1 to 5:1 when the hindered phenol is present.

In an embodiment of the invention, R^3 of the alkylaluminoxane, is a methyl radical and m is from 10 to 40.

The alkylaluminoxanes are typically used in substantial molar excess compared to the amount of group 4 transition metal in the phosphinimine catalyst. The Al^1:group 4 transition metal molar ratios are from 10:1 to 10,000:1, preferably about 30:1 to 500:1.

It is well known in the art, that the alkylaluminoxane can serve dual roles as both an alkylator and an activator. Hence, an alkylaluminoxane activator is often used in combination with activatable ligands such as halogens.

Alternatively, the activator of the present invention may be a combination of an alkylating agent (which may also serve as a scavenger) with an activator capable of ionizing the group 4 metal of the phosphinimine catalyst (i.e. an ionic activator). In this context, the activator can be chosen from one or more alkylaluminoxane and/or an ionic activator.

When present, the alkylating agent may be selected from the group consisting of $(R^4)_pMgX^2_{2-p}$ wherein X^2 is a halide and each R^4 is independently selected from the group consisting of C_{1-10} alkyl radicals and p is 1 or 2; R^4Li wherein in R^4 is as defined above, $(R^4)_qZnX^2_{2-q}$ wherein R^4 is as defined above, X^2 is halogen and q is 1 or 2; $(R^4)_sAl^2X^2_{3-s}$ wherein R^4 is as defined above, X^2 is halogen and s is an integer from 1 to 3. Preferably in the above compounds R^4 is a C_{1-4} alkyl radical, and X^2 is chlorine. Commercially available compounds include triethyl

aluminum (TEAL), diethyl aluminum chloride (DEAC), dibutyl magnesium ($(Bu)_2Mg$), and butyl ethyl magnesium (BuEtMg or BuMgEt).

The ionic activator may be selected from the group consisting of: (i) compounds of the formula $[R^5]^+ [B(R^6)_4]^-$ wherein B is a boron atom, R^5 is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^6 is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with from 3 to 5 substituents selected from the group consisting of a fluorine atom, a C_{1-4} alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula --Si--$(R^7)_3$; wherein each R^7 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and (ii) compounds of the formula $[(R^8)_tZH]^+ [B(R^6)_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^8 is selected from the group consisting of C_{1-8} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^8 taken together with a nitrogen atom may form an anilinium radical and R^6 is as defined above; and (iii) compounds of the formula $B(R^6)_3$ wherein R^6 is as defined above.

In the above compounds preferably R^6 is a pentafluorophenyl radical, and R^5 is a triphenylmethyl cation, Z is a nitrogen atom and R^8 is a C_{1-4} alkyl radical or one R^8 taken together with a nitrogen atom forms an anilinium radical (e.g. $PhR^8_2NH^+$, which is substituted by two R^8 radicals such as for example two C_{1-4} alkyl radicals).

Examples of compounds capable of ionizing the phosphinimine catalyst include the following compounds: triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron,

tributylammonium tetra(pentafluorophenyl)boron, tripropylammonium tetra (o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-trifluoromethylphenyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium tetra (o-tolyl)boron, N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)n-butylboron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron, di-(isopropyl)ammonium tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra (phenyl)boron, triphenylphosphonium tetra)phenyl)boron, tri(methylphenyl)phosphonium tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron, tropillium tetrakispentafluorophenyl borate, triphenylmethylium tetrakispentafluorophenyl borate, benzene (diazonium) tetrakispentafluorophenyl borate, tropillium phenyltris-pentafluorophenyl borate, triphenylmethylium phenyl-trispentafluorophenyl borate, benzene (diazonium) phenyltrispentafluorophenyl borate, tropillium tetrakis (2,3,5,6-tetrafluorophenyl) borate, triphenylmethylium tetrakis (2,3,5,6-tetrafluorophenyl) borate, benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate, tropillium tetrakis (3,4,5-trifluorophenyl) borate, benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate, tropillium tetrakis (1,2,2-trifluoroethenyl) borate, trophenylmethylium tetrakis (1,2,2-trifluoroethenyl) borate, benzene (diazonium) tetrakis (1,2,2-trifluoroethenyl) borate, tropillium tetrakis (2,3,4,5-tetrafluorophenyl) borate, triphenylmethylium tetrakis (2,3,4,5-tetrafluorophenyl) borate, and benzene (diazonium) tetrakis (2,3,4,5-tetrafluorophenyl) borate.

Commercially available activators which are capable of ionizing the group 4 metal of the phosphinimine catalyst include:

N,N-dimethylaniliniumtetrakispentafluorophenyl borate ("$[Me_2NHPh][B(C_6F_5)_4]$"); triphenylmethylium tetrakispentafluorophenyl borate ("$[Ph_3C][B(C_6F_5)_4]$"); and trispentafluorophenyl boron.

The ionic activators compounds may be used in amounts which provide a molar ratio of group 4 transition metal to boron that will be from 1:1 to 1:6.

Optionally, mixtures of alkylaluminoxanes and ionic activators can be used as activators in the polymerization catalyst.

The Inert Support

In the present invention, the phosphinimine catalyst is supported on an inert support. The support used in the present invention can be any support known in the art to be suitable for use with polymerization catalysts. For example the support can be any porous or non porous support material, such as talc, inorganic oxides, inorganic chlorides, aluminophosphates (i.e. $AlPO_4$) and polymer supports (e.g. polystyrene, etc). Preferred supports include Group 2, 3, 4, 5, 13 and 14 metal oxides generally, silica, alumina, silica-alumina, magnesium oxide, magnesium chloride, zirconia, titania, clay (e.g. montmorillonite) and mixtures thereof.

Agglomerate supports such as agglomerates of silica and clay may also be used as a support in the current invention.

Supports are generally used in calcined form. An inorganic oxide support, for example, will contain acidic surface hydroxyl groups which will react with a polymerization catalyst. Prior to use, the inorganic oxide may be dehydrated to remove water and to reduce the concentration of surface hydroxyl groups. Calcination or dehydration of a support is well known in the art. In embodiments of the invention, the support is calcined at temperatures above 200°C, or above 300°C, or above, 400°C, or above 500°C. In other embodiments, the support is

calcined at from about 500 °C to about 1000°C, or from about 600°C to about 900°C. The resulting support may be free of adsorbed water and may have a surface hydroxyl content from about 0.1 to 5 mmol/g of support, or from 0.5 to 3 mmol/g. The amount of hydroxyl groups in a silica support may be determined according to the method disclosed by J. B. Peri and A. L. Hensley Jr., in *J. Phys. Chem.*, 72 (8), 1968, pg 2926.

The support material, especially an inorganic oxide, such as silica, typically has a surface area of from about 10 to about 700 m^2/g, a pore volume in the range from about 0.1 to about 4.0 cc/g and an average particle size of from about 5 to about 500 μm. In a specific embodiment, the support material has a surface a surface area of from about 50 to about 500 m^2/g, a pore volume in the range from about 0.5 to about 3.5 cc/g and an average particle size of from about 10 to about 200 μm. In another specific embodiment the support material has a surface area of from about 100 to about 400 m^2/g, a pore volume in the range from about 0.8 to about 3.0 cc/g and an average particle size of from about 5 to about 100 μm.

The support material, especially an inorganic oxide, such as silica, typically has an average pore size (i.e. pore diameter) of from about 10 to about 1000 Angstroms(Å). In a specific embodiment, the support material has an average pore size of from about 50 to about 500Å. In another specific embodiment, the support material has an average pore size of from about 75 to about 350 Å.

The surface area and pore volume of a support may be determined by nitrogen adsorption according to B.E.T. techniques, which are well known in the art and are described in the *Journal of the American Chemical Society*, 1939, v 60, pg 209-319.

A silica support which is suitable for use in the present invention has a high surface area and is amorphous. By way of example, useful silicas are commercially available under the trademark of Sylopol® 958, 955 and 2408 from Davison Catalysts, a Division of W. R. Grace and Company and ES-70W by PQ Corporation.

Agglomerate supports comprising a clay mineral and an inorganic oxide, may be prepared using a number techniques well known in the art including pelletizing, extrusion, drying or precipitation, spray-drying, shaping into beads in a rotating coating drum, and the like. A nodulization technique may also be used. Methods to make agglomerate supports comprising a clay mineral and an inorganic oxide include spray-drying a slurry of a clay mineral and an inorganic oxide. Methods to make agglomerate supports comprising a clay mineral and an inorganic oxide are disclosed in U.S. Pat. Nos. 6,686,306; 6,399,535; 6,734,131; 6,559,090 and 6,968,375.

An agglomerate of clay and inorganic oxide which may be useful in the current invention may have the following properties: a surface area of from about 20 to about 800 m^2/g, preferably from 50 to about 600 m^2/g; particles with a bulk density of from about 0.15 to about 1 g/ml, preferably from about 0.20 to about 0.75 g/ml; an average pore diameter of from about 30 to about 300 Angstroms (Å), preferably from about 60 to about 150 Å; a total pore volume of from about 0.10 to about 2.0 cc/g, preferably from about 0.5 to about 1.8 cc/g; and an average particle size of from about 4 to 150 microns (μm), preferably from about 8 to 100 microns.

Optionally, a support, for example a silica support, may be treated with one or more salts of the type: $Zr(SO_4)_2 \cdot 4H_2O$, $ZrO(NO_3)_2$, and $Fe(NO_3)_3$ as taught in co-pending Patent Application No. 2,716,772 to the same applicant. Supports that have been otherwise chemically treated are also contemplated for use with the

catalysts and processes of the present invention.

Without wishing to be bound by theory, $Zr(SO_4)_2 \cdot 4H_2O$ and $ZrO(NO_3)_2$ may each act as a source of zirconium oxide (i.e. ZrO_2) which may form for example after calcinations temperatures are employed. Alternately, the $Zr(SO_4)_2 \cdot 4H_2O$ can be used to add $Zr(SO_4)_2$ to an inert support if suitably high calcinations temperatures (those which promote formation of zirconium oxide) are not employed.

The present invention is not limited to any particular procedure for supporting the phosphinimine catalyst or the cocatalyst. Processes for depositing a phosphinimine catalyst complex and/or a cocatalyst on a support are well known in the art (for some non-limiting examples of catalyst supporting methods, see "Supported Catalysts" by James H. Clark and Duncan J. Macquarrie, published online November 15, 2002 in the Kirk-Othmer Encyclopedia of Chemical Technology Copyright © 2001 by John Wiley & Sons, Inc.; for some non-limiting methods to support a single site catalyst see U.S. Pat. No. 5,965,677). For example, the phosphinimine catalyst may be added to a support by co-precipitation with the support material. The cocatalyst can be added to a support before and/or after the phosphinimine catalyst or together with the phosphinimine catalyst (i.e. the phosphinimine catalyst may be mixed with a cocatalyst in a suitable solvent or diluents and the mixture added to a support). Optionally, the cocatalyst can be added to a supported phosphinimine catalyst in situ or on route to a reactor. The phosphinimine catalyst and/or cocatalyst may be slurried or dissolved in a suitable diluent or solvent respectively and then added to a support. Suitable solvents or diluents include but are not limited to hydrocarbons and mineral oil. The phosphinimine catalyst may be added to the solid support, in the form of a solid, solution or slurry, followed by the addition of the cocatalyst in solid form or as a

solution or slurry. The cocatalyst may be added to the solid support, in the form of a solid, solution or slurry, followed by the addition of the phosphinimine catalyst in solid form or as a solution or slurry. Phosphinimine catalyst, cocatalyst, and support can be mixed together in the presence or absence of a diluents or solvent, but use of diluent(s) or solvent(s) is preferred.

The loading of the phosphinimine catalyst on the support is not specifically defined, but by way of non limiting example can be from about 0.005 to 1.0, or from about 0.010 to 0.50, or from about 0.015 to 0.40, or from about 0.015 to 0.035 mmol of the phosphinimine catalyst per gram of support. In further embodiments of the invention, the loading of the phosphinimine catalyst on the support may from about 0.020 to 0.031 mmol, or from about 0.025 to 0.0305 mmol of the phosphinimine catalyst per gram of support.

In embodiments of the invention, the phosphinimine catalyst will be added to the inert support so as to give from 0.01 to 10 wt% of Ti, or from 0.05 to 5.0 wt% of Ti, or from 0.05 to 3.0 wt% of Ti, or from 0.10 to 2.0 wt% of Ti based on the combined weight of the phosphinimine catalyst, the inert support and the cocatalyst.

The phosphinimine based (olefin) polymerization catalyst may be fed to a reactor system in a number of ways. The polymerization catalyst may be fed to a reactor in dry mode using a dry catalyst feeder, examples of which are well known in the art. Alternatively, the polymerization catalyst may be fed to a reactor as a slurry in a suitable diluent. Suitable solvents or diluents are inert hydrocarbons well known to persons skilled in the art and generally include aromatics, paraffins, and cycloparaffinics such as for example benzene, toluene, xylene, cyclohexane, fuel oil, isobutane, mineral oil, kerosene and the like. Further specific examples include but are not limited to hexane, heptanes, isopentane and mixtures thereof. Solvents

which will not extract appreciable amounts of the phosphinimine catalyst, the cocatalyst or the catalyst modifier away from the inert support are preferred. The (olefin) polymerization catalyst components, which include at least one phosphinimine catalyst, at least one support, at least one cocatalyst, and optionally at least one catalyst modifier, may be combined offline and prior to their addition to a polymerization zone, or they may be combined on route to a polymerization zone.

The Polymerization Process

Olefin polymerization processes which are compatible with the current invention include gas phase and slurry phase polymerization processes, with gas phase processes being preferred. Preferably, ethylene copolymerization with an alpha-olefin is carried out in the gas phase, in for example a fluidized bed reactor.

Detailed descriptions of slurry polymerization processes are widely reported in the patent literature. For example, particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution is described in U.S. Pat. No. 3,248,179. Slurry processes include those employing a loop reactor and those utilizing a single stirred reactor or a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Further examples of slurry processes are described in U.S. Patent No. 4,613,484.

Slurry processes are conducted in the presence of a hydrocarbon diluent such as an alkane (including isoalkanes), an aromatic or a cycloalkane. The diluent may also be the alpha olefin comonomer used in copolymerizations. Alkane diluents include propane, butanes, (i.e. normal butane and/or isobutane), pentanes, hexanes, heptanes and octanes. The monomers may be soluble in (or miscible with) the diluent, but the polymer is not (under polymerization conditions). The

polymerization temperature is preferably from about 5°C to about 200°C, most preferably less than about 120°C typically from about 10°C to 100°C. The reaction temperature is selected so that an ethylene copolymer is produced in the form of solid particles. The reaction pressure is influenced by the choice of diluent and reaction temperature. For example, pressures may range from 15 to 45 atmospheres (about 220 to 660 psi or about 1500 to about 4600 kPa) when isobutane is used as diluent (see, for example, U.S. Patent No. 4,325,849) to approximately twice that (*i.e.* from 30 to 90 atmospheres – about 440 to 1300 psi or about 3000-9100 kPa) when propane is used (see U.S. Patent No. 5,684,097). The pressure in a slurry process must be kept sufficiently high to keep at least part of the ethylene monomer in the liquid phase. The reaction typically takes place in a jacketed closed loop reactor having an internal stirrer (e.g. an impeller) and at least one settling leg. Catalyst, monomers and diluents are fed to the reactor as liquids or suspensions. The slurry circulates through the reactor and the jacket is used to control the temperature of the reactor. Through a series of let down valves the slurry enters a settling leg and then is let down in pressure to flash the diluent and unreacted monomers and recover the polymer generally in a cyclone. The diluent and unreacted monomers are recovered and recycled back to the reactor.

A gas phase process is commonly carried out in a fluidized bed reactor. Such gas phase processes are widely described in the literature (see for example U.S. Pat. Nos 4,543,399; 4,588,790; 5,028,670; 5,317,036; 5,352,749; 5,405,922; 5,436,304; 5,433,471; 5,462,999; 5,616,661 and 5,668,228). In general, a fluidized bed gas phase polymerization reactor employs a "bed" of polymer and catalyst which is fluidized by a flow of monomer and other optional components which are at least partially gaseous. Heat is generated by the enthalpy of polymerization of the

monomer (and optional comonomer(s)) flowing through the bed. Un-reacted monomer and other optional gaseous components exit the fluidized bed and are contacted with a cooling system to remove this heat. The cooled gas stream, including monomer, and optional other components (such as condensable liquids), is then re-circulated through the polymerization zone, together with "make-up" monomer to replace that which was polymerized on the previous pass. Simultaneously, polymer product is withdrawn from the reactor. As will be appreciated by those skilled in the art, the "fluidized" nature of the polymerization bed helps to evenly distribute/mix the heat of reaction and thereby minimize the formation of localized temperature gradients.

The reactor pressure in a gas phase process may vary from about atmospheric to about 600 Psig. In another embodiment, the pressure can range from about 100 psig (690 kPa) to about 500 psig (3448 kPa). In yet another embodiment, the pressure can range from about 200 psig (1379 kPa) to about 400 psig (2759 kPa). In still another embodiment, the pressure can range from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

The reactor temperature in a gas phase process may vary according to the heat of polymerization as described above. In a specific embodiment, the reactor temperature can be from about 30°C to about 130°C. In another specific embodiment, the reactor temperature can be from about 60°C to about 120°C. In yet another specific embodiment, the reactor temperature can be from about 70°C to about 110°C. In still yet another specific embodiment, the temperature of a gas phase process can be from about 70°C to about 100°C.

The fluidized bed process described above is well adapted for the preparation of polyethylene and polyethylene copolymers. Hence, monomers and

comonomers include ethylene and C_{3-12} alpha olefins which are unsubstituted or substituted by up to two C_{1-6} hydrocarbyl radicals; C_{8-12} vinyl aromatic olefins which are unsubstituted or substituted by up to two substituents selected from the group consisting of C_{1-4} hydrocarbyl radicals; and C_{4-12} straight chained or cyclic diolefins which are unsubstituted or substituted by a C_{1-4} hydrocarbyl radical. Illustrative non-limiting examples of alpha-olefins that may be copolymerized with ethylene include one or more of propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, and 1-decene, styrene, alpha methyl styrene, p-t-butyl styrene, and the constrained-ring cyclic olefins such as cyclobutene, cyclopentene, dicyclopentadiene norbornene, hydrocarbyl -substituted norbornenes, alkenyl-substituted norbornenes and the like (e.g. 5-methylene-2-norbornene and 5-ethylidene-2-norbornene, bicyclo-(2,2,1)-hepta-2,5-diene).

In an embodiment, the invention is directed toward a polymerization process involving the polymerization of one or more of the monomer(s) and comonomer(s) including ethylene alone or in combination with one or more linear or branched comonomer(s) having from 3 to 30 carbon atoms, preferably 3-12 carbon atoms, more preferably 4 to 8 carbon atoms. The process is particularly well suited to copolymerization reactions involving polymerization of ethylene in combination with one or more of the comonomers, for example, the alpha-olefins: propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, styrene and cyclic and polycyclic olefins such as cyclopentene, norbornene and cyclohexene or a combination thereof. Other comonomers for use with ethylene can include polar vinyl monomers, diolefins such as 1,3-butadiene, 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, norbornadiene, and other unsaturated monomers including acetylene and aldehyde monomers. Higher alpha-olefins and polyenes or

macromers can be used also. Preferably the comonomer is an alpha-olefin having from 3 to 15 carbon atoms, preferably 4 to 12 carbon atoms and most preferably 4 to 10 carbon atoms.

In an embodiment of the present invention, ethylene is copolymerized with an alpha olefin having from 3-10 carbon atoms and ethylene makes up at least 75 wt% of the total olefin feed entering the reactor.

In an embodiment of the present invention, ethylene is copolymerized with an alpha olefin having from 3-10 carbon atoms and ethylene makes up at least 85 wt% of the total olefin feed entering the reactor.

In embodiments of the present invention, ethylene is copolymerized with propylene, 1-butene, 1-hexene or 1-octene.

In an embodiment of the present invention, ethylene is copolymerized with 1-butene and ethylene makes up at least 75 weight% (i.e. wt%) of the total olefin feed entering the reactor.

In an embodiment of the present invention, ethylene is copolymerized with 1-hexene and ethylene makes up at least 75 wt% of the total olefin feed entering the reactor.

In an embodiment of the present invention, ethylene is copolymerized with 1-hexene and ethylene makes up at least 85 wt% of the total olefin feed entering the reactor.

Gas phase fluidized bed polymerization processes may employ a polymer seed bed in the reactor prior to initiating the polymerization process. It is contemplated by the current invention to use a polymer seed bed that has been treated with a catalyst modifier or an optional scavenger (see below). In addition,

the polymer products obtained by using the catalysts and processes of the current invention may themselves be used as polymer seed bed materials.

Optional Scavenger

Optionally, scavengers are added to the polymerization process. The present invention can be carried out in the presence of any suitable scavenger or scavengers. Scavengers are well known in the art.

In an embodiment of the invention, scavengers are organoaluminum compounds having the formula: $Al^3(X^3)_n(X^4)_{3-n}$, where (X^3) is a hydrocarbyl having from 1 to about 20 carbon atoms; (X^4) is selected from alkoxide or aryloxide, any one of which having from 1 to about 20 carbon atoms; halide; or hydride; and n is a number from 1 to 3, inclusive; or hydrocarbyl aluminoxanes having the formula:

$R^3_2Al^1O(R^3Al^1O)_mAl^1R^3_2$

wherein each R^3 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 3 to 50. Some non-limiting preferred scavengers useful in the current invention include triisobutylaluminum, triethylaluminum, trimethylaluminum or other trihydrocarbyl aluminum compounds.

The scavenger may be used in any suitable amount but by way of non-limiting examples only, can be present in an amount to provide a molar ratio of Al:M (where M is the metal of the organometallic compound) of from about 20 to about 2000, or from about 50 to about 1000, or from about 100 to about 500. Generally the scavenger is added to the reactor prior to the polymerization catalyst and in the absence of additional poisons and over time declines to 0, or is added continuously.

Optionally, the scavengers may be independently supported. For example, an inorganic oxide that has been treated with an organoaluminum compound or hydrocarbyl aluminoxane may be added to the polymerization reactor. The method

of addition of the organoaluminum or hydrocarbyl aluminoxane compounds to the support is not specifically defined and is carried out by procedures well known in the art.

A scavenger may optionally be added to the catalyst modifier prior to feeding the catalyst modifier to a reactor or prior to combining the catalyst modifier with the polymerization catalyst (or one or more polymerization catalyst components). Alternatively a scavenger may be combined with the catalyst modifier on route to a polymerization reactor.

Polymer

The polymer compositions made using the present invention are most preferably copolymers of ethylene and an alpha olefin selected from 1-butene, 1-hexene and 1-octene.

In embodiments of the invention, the copolymer composition will comprise at least 75 weight% of ethylene units, or at least 80 wt% of ethylene units, or at least 85 wt% of ethylene units with the balance being an alpha-olefin unit, based on the weight of the copolymer composition.

Polymer properties such as average molecular weight (e.g. Mw, Mn and Mz), molecular weight distribution (i.e. Mw/Mn), density, melt indices (e.g. I_2, I_5, I_{21}, I_{10}), melt index or melt flow ratios (e.g. I_{21}/I_2, I_{21}/I_5), comonomer distribution breadth index (CDBI), TREF-profile, comonomer distribution profile, and the like as these terms are defined further below and in for example co-pending CA Application No. 2,734,167 (to the same Applicant) are not specifically defined, but by way of non-limiting example only, the polymer compositions made using the present invention, may have a density of from 0.910 g/cc to 0.93 g/cc, a melt index of from 0.5 to 10.0

g/10min, a melt flow ratio (I_{21}/I_2) of from 14 to 18, a weight average molecular weight of from 40,000 to 140,000, and a unimodal or bimodal TREF profile.

Composition Distribution

Indices which characterize changes in composition distribution of the ethylene copolymer include changes to one or more of the following:

A) the composition distribution breadth index (CDBI) of the ethylene copolymer as measured using temperature rising elution fractionation (TREF) methods;

B) the weight percent of a higher temperature eluting material (i.e. from 90°C to 105°C) observed in TREF profile obtained for the ethylene copolymer; and

C) the comonomer distribution profile (i.e. the comonomer incorporation relative to molecular weight) in the ethylene copolymer as measured by gel permeation chromatography with Fourier transform infra-red detection (GPC-FTIR).

In the present invention, the composition distribution of an ethylene copolymer is altered by changing at least one of the following: a) the amount of a catalyst modifier fed to a reactor; b) the amount of catalyst modifier included in a polymerization catalyst.

In embodiments of the invention, the amount of catalyst modifier fed to a reactor is changed by at least 1 ppm (based on the weight of the copolymer produced), preferably least 2.5 ppm, or at least 5 ppm, or at least 10 ppm, or at least 20 ppm, or at least 25 ppm.

In embodiments of the invention, the amount of catalyst modifier fed to a reactor is changed by from 1 to 100 ppm and including smaller ranges within this range, such as but not limited to, from 5 to 75 ppm, or from 5 to 50 ppm, or from 5 to

40, or from 5 to 30 ppm, or from 5 to 25 ppm, or from 5 to 20 ppm, or from 5 to 15 ppm, or from 5 to 10 ppm, or from 1 to 25 ppm, or from 1 to 20 ppm or from 1 to 15 ppm or from 1 to 10 ppm, or from 1 to 5 ppm (based on the weight of the copolymer produced).

In embodiments of the invention, the amount of catalyst modifier included in the polymerization catalyst is changed by at least 0.1 wt% (based on the combined weight of the phosphinimine catalyst, the inert support and the cocatalyst), preferably at least 0.25 wt%, or at least 0.5 wt%, or at least 0.75wt%, or at least 1.0 wt%, or at least 1.5 wt%, or at least 2.0 wt%, or at least 2.5 wt%, or at least 3.0 wt%, or at least 3.5 wt%.

In embodiments of the invention, the amount of catalyst modifier included in the polymerization catalyst is changed by from 0.1 to 10 wt% and including smaller ranges within this range, such as but not limited to, from 0.25 to 5.0 wt%, or from 0.5 to 5.0 wt%, or from 0.25 to 4.5 wt%, or from 0.5 to 4.5 wt%, or from 0.25 to 4.0 wt%, or from 0.5 to 4.0 wt%, or from 0.25 to 3.5 wt%, or from 0.5 to 3.0 wt%, or from 0.25 to 3.0 wt%, or from 0.25 to 2.5 wt%, or from 0.25 to 2.0 wt%, or from 0.25 to 1.5 wt%, or from 0.25 to 1.25 wt%, or from 0.25 to 1.0 wt% (based on the combined weight of the phosphinimine catalyst, the inert support and the cocatalyst).

In an embodiment of the invention, altering at least one of the following: a) the amount of catalyst modifier fed to a gas phase reactor; b) the amount of catalyst modifier present in the polymerization catalyst; changes the composition distribution of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, altering at least one of the following: a) the amount of catalyst modifier fed to a gas phase reactor by 1 ppm or more; b) the amount of catalyst modifier present in the polymerization catalyst by 0.25 wt% or

more; changes the composition distribution of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, the composition distribution of an ethylene copolymer is altered by polymerizing ethylene and at least one alpha-olefin in a gas phase reactor in the presence of a polymerization catalyst by changing at least one of the following: a) an amount of catalyst modifier fed to the reactor by at least 2.5 ppm; b) an amount of catalyst modifier present in the polymerization catalyst by at least 0.25 wt%; where the polymerization catalyst comprises a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, the composition distribution of an ethylene copolymer is altered by polymerizing ethylene and at least one alpha-olefin in a gas phase reactor in the presence of a polymerization catalyst by changing at least one of the following: a) an amount of catalyst modifier fed to the reactor by at least 5 ppm; b) an amount of catalyst modifier present in the polymerization catalyst by at least 0.5 wt%; where the polymerization catalyst comprises a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, the composition distribution of an ethylene copolymer is altered by polymerizing ethylene and at least one alpha-olefin in a gas phase reactor in the presence of a polymerization catalyst by changing at least one of the following: a) an amount of catalyst modifier fed to the reactor by at least 5 ppm; b) an amount of catalyst modifier present in the polymerization catalyst by at least 1.0 wt%; where the polymerization catalyst comprises a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, the composition distribution of an ethylene copolymer is altered by polymerizing ethylene and at least one alpha-olefin in a gas

phase reactor in the presence of a polymerization catalyst by changing at least one of the following: a) an amount of catalyst modifier fed to the reactor by at least 10 ppm; b) an amount of catalyst modifier present in the polymerization catalyst by at least 1.5 wt%; where the polymerization catalyst comprises a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, the composition distribution of an ethylene copolymer is altered using a method comprising: i) introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising a phosphinimine catalyst, an inert support, and a cocatalyst; feeding from 0 to 100 ppm of a catalyst modifier into the reactor (based on the weight of copolymer produced), the catalyst modifier comprising a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the reactor to give the ethylene copolymer; wherein the composition distribution of the ethylene copolymer is altered by changing the amount of the catalyst modifier fed to the reactor by at least 5 ppm (based on the weight of copolymer produced).

In an embodiment of the invention, the composition distribution of an ethylene copolymer is altered using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst; and further including from 0 to 10 weight percent of a catalyst modifier based on the weight of i), ii) and iii) of the polymerization catalyst, the catalyst modifier comprising a compound having

the formula $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer; wherein the composition distribution of the ethylene copolymer is altered by changing the amount of the catalyst modifier included in the olefin polymerization catalyst by at least 0.25 weight percent (based on the weight of i), ii), and iii) of the polymerization catalyst).

In an embodiment of the invention the composition distribution of an ethylene copolymer, is altered using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 wt% of a catalyst modifier (based on the weight of the polymerization catalyst); feeding from 0 to 100 ppm of a catalyst modifier into the gas phase reactor (based on the weight of copolymer produced); and polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer; wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor comprise a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and wherein the composition distribution of the ethylene copolymer is altered by changing at least one of the following: a) the amount of the catalyst modifier fed into the gas

phase reactor by at least 5 ppm (based on the weight of copolymer produced); b) the amount the catalyst modifier included in the polymerization catalyst by at least 0.5 wt% (based on the weight of i), ii) and iii) of the polymerization catalyst).

In an embodiment of the invention, the catalyst modifier included in the polymerization catalyst comprises a different type of long chain amine compound than the catalyst modifier fed into the gas phase reactor.

In an embodiment of the invention, the catalyst modifier included in the polymerization catalyst comprises the same type of long chain amine compound which is fed into the gas phase reactor.

In embodiments of the invention, the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor are different types of long chain dialkanolamines or the same the type of long chain dialkanolamines.

A) Composition Distribution Breadth Index (CDBI). Ethylene copolymers can be defined by a composition distribution breadth index (CDBI), which is a measure of how comonomers are distributed (i.e. the "composition distribution") in an ethylene copolymer. The definition of composition distribution breadth index (CDBI) can be found in U.S. Pat. No. 5,206,075 and PCT publication WO 93/03093. The CDBI is conveniently determined using techniques which isolate polymer fractions based on their solubility (and hence their comonomer content). For example, temperature rising elution fractionation (TREF) as described by Wild et al. J. Poly. Sci., Poly. Phys. Ed. Vol. 20, p441, 1982 can be employed. From the weight fraction versus composition distribution curve, the CDBI is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median.

Generally, ethylene copolymers with a CDBI of less than about 50%, are considered "heterogeneously branched" copolymers with respect to short chain branching. Such heterogeneously branched materials may include a highly branched fraction, a medium branched fraction and a higher density fraction having little or no short chain branching. In contrast, ethylene copolymers with a CDBI of greater than about 50% are considered "homogeneously branched" copolymers, with respect to short chain branching, in which the majority of polymer chains may have a similar degree of branching.

In an embodiment of the invention, the composition distribution breadth index (CDBI) of an ethylene copolymer is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor; b) the amount of catalyst modifier included in the polymerization catalyst.

In an embodiment of the invention, the composition distribution breadth index (CDBI) of an ethylene copolymer is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 5 ppm or more; b) the amount of catalyst modifier included in the polymerization catalyst by 0.25 wt% or more.

In an embodiment of the invention, the composition distribution breadth index (CDBI) of an ethylene copolymer is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 5 ppm or more; b) the amount of catalyst modifier included in the polymerization catalyst by 0.5 wt% or more.

In an embodiment of the invention, the composition distribution breadth index (CDBI) of an ethylene copolymer is altered by more than 1% by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 10 ppm

or more; b) the amount of catalyst modifier included in the polymerization catalyst by 1.0 wt% or more.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor changes the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) changes the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 10 ppm (based on the weight of copolymer produced) changes the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) increases the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) decreases the composition distribution breadth index (as

measured by TREF) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor changes the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made in the presence of 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) changes the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, increasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) increases the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, decreasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) decreases the composition distribution breadth index (as measured by TREF) of an ethylene copolymer made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In embodiments of the invention, an ethylene copolymer made in the presence of from 15 to 35 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with a polymerization catalyst comprising: i) a phosphinimine catalyst, ii) an inert support, and iii) a cocatalyst; has an at least 3%, or at least 5%, or at least 7% higher comonomer distribution breadth index (as measured by TREF) than an ethylene copolymer made in the absence of catalyst modifier (directly added to the reactor) with a catalyst comprising: i) a phosphinimine catalyst, ii) an inert support, and iii) a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) changes the comonomer distribution breadth index (as measured by TREF) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst,

ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.50 weight%, changes the comonomer distribution breadth index (as measured by TREF) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, increases the comonomer distribution breadth index (as measured by TREF) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, decreases the comonomer distribution breadth index (as measured by TREF) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, changes the comonomer distribution breadth index (as measured by TREF) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst,

ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 1.0 weight%, increases the comonomer distribution breadth index (as measured by TREF) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 1.0 weight%, decreases the comonomer distribution breadth index (as measured by TREF) of an ethylene copolymer made with the polymerization catalyst.

In embodiments of the invention, an ethylene copolymer made with a polymerization catalyst comprising: i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst, and further including from 0.5 to 4.5 wt% of a catalyst modifier (based on the weight of the polymerization catalyst); has an at least 3%, or at least 5%, or at least 7% higher comonomer distribution breadth index (as measured by TREF) than an ethylene copolymer made with a catalyst comprising: i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst, but no catalyst modifier.

In an embodiment of the invention, the composition distribution breadth index (CDBI) of an ethylene copolymer is altered using a method comprising: i) introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising a phosphinimine catalyst, an inert support, and a cocatalyst; feeding from 0 to 100 ppm of a catalyst modifier into the reactor (based on the weight of copolymer produced), the catalyst modifier comprising a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to

30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the reactor to give the ethylene copolymer; wherein the composition distribution breadth index (CDBI) of the ethylene copolymer is altered by changing the amount of the catalyst modifier fed to the reactor by at least 5 ppm (based on the weight of copolymer produced).

In an embodiment of the invention, the composition distribution breadth index (CDBI) of an ethylene copolymer is altered using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst; and further including from 0 to 10 weight percent of a catalyst modifier based on the weight of i), ii) and iii) of the polymerization catalyst, the catalyst modifier comprising a compound having the formula $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer; wherein the composition distribution breadth index (CDBI) of the ethylene copolymer is altered by changing the amount of the catalyst modifier included in the olefin polymerization catalyst by at least 0.25 weight percent (based on the weight of the polymerization catalyst).

In an embodiment of the invention the composition distribution breadth index (CDBI) of an ethylene copolymer, is altered using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst

comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 wt% of a catalyst modifier; feeding from 0 to 100 ppm of a catalyst modifier into the gas phase reactor (based on the weight of the copolymer produced); and polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer; wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor comprise a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and wherein the composition distribution breadth index (CDBI) of the ethylene copolymer is altered by changing at least one of the following: a) the amount of the catalyst modifier fed into the gas phase reactor by at least 5 ppm (based on the weight of copolymer produced); b) the amount the catalyst modifier included in the polymerization catalyst by at least 0.5 wt% (based on the weight of i), ii) and iii) of the polymerization catalyst).

B) The Weight Percent of a High Temperature Eluting Material. An ethylene copolymer can be defined by a weight percent of a higher temperature eluting material or fraction (i.e. from 90°C to 105°C) observed in TREF profile. The amount of copolymer which elutes at a temperature of from 90°C to 105 °C is another indication as to how comonomers are distributed (i.e. the "composition distribution") in an ethylene copolymer.

In an embodiment of the invention, the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis is altered by changing at least one of the

following: i) the amount of catalyst modifier fed to the reactor; ii) the amount of catalyst modifier present in the polymerization catalyst.

In an embodiment of the invention, the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 5 ppm or more; b) the amount of catalyst modifier present in the polymerization catalyst by 0.25 wt% or more.

In an embodiment of the invention, the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 5 ppm or more; b) the amount of catalyst modifier present in the polymerization catalyst by 0.5 wt% or more.

In an embodiment of the invention, the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis is altered by at least 1%, by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 10 ppm or more; b) the amount of catalyst modifier present in the polymerization catalyst by 1.0 wt% or more.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made with an olefin

polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 10 ppm (based on the weight of copolymer produced) changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) decreases the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) increases the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C

in a TREF analysis where the copolymer is made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor (based on the weight of copolymer produced) changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, increasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) decreases the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made in the presence 0 to 100 ppm of catalyst

modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, decreasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) increases the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis where the copolymer is made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In embodiments of the invention, an ethylene copolymer made in the presence of from 15 to 35 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with a polymerization catalyst comprising: i) a phosphinimine catalyst, ii) an inert support, and iii) a cocatalyst; has a weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis which is at least 1%, or at least 2% or by at least 3% higher than in an ethylene copolymer made with a catalyst comprising: i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst, but in the absence of catalyst modifier (being fed to the reactor).

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst,

ii) an inert support, iii) a cocatalyst and further including from 0 to 10 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, decreases the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, increases the weight percent of an ethylene copolymer

fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, changes the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 1.0 weight%, decreases the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 1.0 weight%, increases the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer made with the polymerization catalyst.

In embodiments of the invention, and ethylene copolymer made with a polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support,

iii) a cocatalyst and further including 0.5 to 4.5 weight percent of a catalyst modifier (based on the weight of the polymerization catalyst) has an at least 1%, 2%, or 3% lower weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis than an ethylene copolymer made with a polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst, but no catalyst modifier.

In an embodiment of the invention, the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer is changed using a method comprising: i) introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising a phosphinimine catalyst, an inert support, and a cocatalyst; feeding from 0 to 100 ppm of a catalyst modifier into the reactor (based on the weight of copolymer produced), the catalyst modifier comprising a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the reactor to give the ethylene copolymer; wherein the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of the ethylene copolymer is altered by changing the amount of the catalyst modifier fed to the reactor by at least 5 ppm (based on the weight of copolymer produced).

In an embodiment of the invention, the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from

90°C to 105°C in a TREF analysis of an ethylene copolymer is changed using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst; and further including from 0 to 10 weight percent of a catalyst modifier based on the weight of i), ii) and iii) of the polymerization catalyst, the catalyst modifier comprising a compound having the formula $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer; wherein the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of the ethylene copolymer is altered by changing the amount of the catalyst modifier included in the olefin polymerization catalyst by at least 0.25 weight percent (based on the weight of the polymerization catalyst).

In an embodiment of the invention, the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of an ethylene copolymer is changed using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 wt% of a catalyst modifier (based on the weight of the polymerization catalyst); feeding from 0 to 100 ppm of a catalyst modifier into the gas phase reactor (based on the weight of the copolymer produced); and polymerizing ethylene and an alpha-olefin in the gas phase reactor

to give the ethylene copolymer; wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor comprise a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and wherein the weight percent of an ethylene copolymer fraction (based on the weight of the copolymer) which elutes at from 90°C to 105°C in a TREF analysis of the ethylene copolymer is altered by changing at least one of the following: a) the amount of the catalyst modifier fed into the gas phase reactor by at least 5 ppm (based on the weight of copolymer produced); b) the amount the catalyst modifier included in the polymerization catalyst by at least 0.5 wt% (based on the weight of i), ii) and iii) of the polymerization catalyst).

C) Comonomer Distribution Profile. Ethylene copolymers can have a number of different comonomer distribution profiles which represent how the comonomers are distributed amongst polymer chains of different molecular weights and hence are an indication of the "composition distribution". The comonomer distribution profile is most typically measured using Gel-Permeation Chromatography with Fourier Transform Infra-Red detection (GPC-FTIR). If the comonomer incorporation decreases with molecular weight, as measured using GPC-FTIR, the distribution is described as "normal" or "negative". If the comonomer incorporation is approximately constant with molecular weight, as measured using GPC-FTIR, the comonomer distribution is described as "flat". The terms "reversed comonomer distribution" and "partially reversed comonomer distribution" mean that

in the GPC-FTIR data obtained for the copolymer, there is one or more higher molecular weight components having a higher comonomer incorporation than in one or more lower molecular weight segments. If the comonomer incorporation rises with molecular weight, the distribution is described as "reversed". Where the comonomer incorporation rises with increasing molecular weight and then declines, the comonomer distribution is described as "partially reversed".

In an embodiment of the invention, the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor; b) the amount of catalyst modifier present in the polymerization catalyst.

In an embodiment of the invention, the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 5 ppm or more; b) the amount of catalyst modifier present in the polymerization catalyst by 0.25 wt% or more.

In an embodiment of the invention, the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 5 ppm or more; b) the amount of catalyst modifier present in the polymerization catalyst by 0.5 wt% or more.

In an embodiment of the invention, the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer is altered by changing at least one of the following: a) the amount of catalyst modifier fed to the reactor by 10 ppm or more; b) the amount of catalyst modifier present in the polymerization catalyst by 1.0 wt% or more.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor changes the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) changes the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 10 ppm (based on the weight of copolymer produced) changes the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) increases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) decreases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR)

in an ethylene copolymer made with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, and a cocatalyst.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor (based on the weight of copolymer produced) changes the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, altering the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) changes the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, increasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) increases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a

phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, decreasing the amount of catalyst modifier fed to a polymerization reactor by at least 5 ppm (based on the weight of copolymer produced) decreases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made in the presence 0 to 100 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with an olefin polymerization catalyst comprising: a phosphinimine catalyst, an inert support, a cocatalyst and optionally a catalyst modifier.

In an embodiment of the invention, an ethylene copolymer made in the presence of from 15 to 35 ppm of catalyst modifier (i.e. the total amount of catalyst modifier fed directly to the reactor, based on the weight of copolymer produced) with a polymerization catalyst comprising: i) a phosphinimine catalyst, ii) an inert support, and iii) a cocatalyst; increases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made with the polymerization catalyst when compared to an ethylene copolymer made with the same polymerization catalyst in the in the absence of catalyst modifier (added directly to the reactor).

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) changes the

comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, changes the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6.0 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, increases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 6 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, decreases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, altering the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a

catalyst modifier (based on the weight of the polymerization catalyst) by at least 0.5 weight%, changes the comonomer distribution profile (as measured by GPC-FTIR) of an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, increasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 1.0 weight%, increases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, decreasing the amount of catalyst modifier present in an olefin polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 4.5 weight% of a catalyst modifier (based on the weight of the polymerization catalyst) by at least 1.0 weight%, decreases the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) in an ethylene copolymer made with the polymerization catalyst.

In an embodiment of the invention, an ethylene copolymer made with a polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst, and further including from 0.5 to 4.5 wt% of a catalyst modifier (based on the weight of the polymerization catalyst); has an increased amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) when compared to an ethylene copolymer made with a polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst, but no catalyst modifier.

In embodiments of the invention, inclusion of from 0.5 to 4.5 wt% of a catalyst modifier in the polymerization catalyst changes the comonomer incorporation profile of an ethylene copolymer from a normal profile to a flat profile, or from a flat profile to a reversed profile, or from a normal profile to a reversed profile.

In an embodiment of the invention, the comonomer distribution profile of an ethylene copolymer is changed using a method comprising: i) introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising a phosphinimine catalyst, an inert support, and a cocatalyst; feeding from 0 to 100 ppm of a catalyst modifier into the reactor (based on the weight of copolymer produced), the catalyst modifier comprising a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the reactor to give the ethylene copolymer; wherein the comonomer distribution profile of the ethylene copolymer is altered by changing the amount of the catalyst modifier fed to the reactor by at least 5 ppm (based on the weight of copolymer produced).

In an embodiment of the invention, the comonomer distribution profile of an ethylene copolymer is changed using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst; and further including from 0 to 10 weight percent of a catalyst modifier based on the weight of i), ii) and iii) of the polymerization catalyst, the catalyst modifier comprising a compound having the formula $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl

group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer; wherein the comonomer distribution profile of the ethylene copolymer is altered by changing the amount of the catalyst modifier included in the olefin polymerization catalyst by at least 0.25 weight percent (based on the weight of the polymerization catalyst).

In an embodiment of the invention, the comonomer distribution profile of an ethylene copolymer is changed using a method comprising: introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 wt% of a catalyst modifier (based on the weight of the polymerization catalyst); feeding from 0 to 100 ppm of a catalyst modifier into the gas phase reactor (based on the weight of copolymer produced); and polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer; wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor comprise a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and wherein the comonomer distribution profile of the ethylene copolymer is altered by changing at least one of the following: a) the amount of the catalyst modifier fed into the gas phase reactor by at least 5 ppm (based on the weight of copolymer

produced); b) the amount the catalyst modifier included in the polymerization catalyst by at least 0.5 wt% (based on the weight of *i*), *ii*) and *iii*) of the polymerization catalyst).

Gels

Changes in the amount of catalyst modifier added to a reactor or included in the polymerization catalyst may also change the number of gels present in films made from ethylene copolymers produced with the polymerization catalyst. Without wishing to be bound by theory, the change in gel count is likely a result of changing the polymer architecture as represented by the "composition distribution" which is already discussed above.

In an embodiment of the invention, the inclusion of from 0.5 to 4.5 weight per cent of a catalyst modifier in the polymerization catalyst decreases the number of gels present (by OCS gel count) in a film cast from a copolymer obtained using the polymerization catalyst (relative to film cast from a copolymer obtained using a polymerization catalyst not treated with a catalyst modifier).

In embodiments of the invention, the inclusion of from 0.5 to 4.5 weight per cent of a catalyst modifier in the polymerization catalyst decreases the number of gels present in a film cast from a copolymer obtained using the olefin polymerization catalyst, from above 100 to below 10, or from above 50 to below 10, or from above 20 to below 10 according to OCS gel count (relative to film cast from a copolymer obtained using a polymerization catalyst not treated with a catalyst modifier).

In an embodiment of the invention, the addition of a catalyst modifier to a gas phase polymerization reactor decreases the number of gels present in a film cast from a copolymer obtained using a polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support and iii) a cocatalyst.

In embodiments of the current invention, altering the composition distribution of an ethylene copolymer, changes the number of gels present in a film cast from the ethylene copolymer. Methods to alter the composition distribution of an ethylene copolymer and hence the number of gels present in a film cast from the ethylene copolymer are already discussed above.

EXAMPLES

Catalyst Modifier

Atmer-163™ was obtained from CRODA CANADA LTD and dried over 3Å molecular sieves for several days prior to use. Atmer-163 has as its main component, a mixture of C13 to C15 hydrocarbyl diethanolamines, $CH_3(CH_2)_xN(CH_2CH_2OH)_2$ where x is 12 to 14.

Armostat-1800™ was obtained from Akzo Nobel and purified by drying a toluene or pentane solution over 3 Å molecular sieves for several days prior to use. Armostat-1800 is principally a long chain substituted alkanolamine having the formula: $C_{18}H_{37}N(CH_2CH_2OH)_2$.

Polymerization Catalysts

All reactions involving air and or moisture sensitive compounds were conducted under nitrogen using standard Schlenk and cannula techniques, or in a glovebox. Reaction solvents were purified either using the system described by Pangborn et. al. in *Organometallics* 1996, v*15*, p.1518 or used directly after being stored over activated 4 Å molecular sieves. The aluminoxane used was a 10% MAO solution in toluene supplied by Albemarle which was used as received. The support used was silica Sylopol 2408 obtained from W.R. Grace. & Co. The support was calcined by fluidizing with air at 200 °C for 2 hours followed by nitrogen at 600°C for 6 hours and stored under nitrogen. The phosphinimine catalyst

compound (1,2-(n-propyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl_2 was made in a manner similar to the procedure given in U.S. Pat. No. 7,531,602 (see Example 2).

Type 1 Polymerization Catalyst (Comparative: without catalyst modifier present): To a slurry of dehydrated silica (361.46 g) in toluene (1400 mL) was added a 10 wt% MAO solution (1004.41 g of 4.5 wt% Al in toluene) over 35 minutes. The vessel containing the MAO was rinsed with toluene (2 x 50 mL) and added to the reaction mixture. The resultant slurry was stirred with an overhead stirrer assembly (200 rpm) for 2 hours at ambient temperature. To this slurry was added a toluene (~100 mL) solution of (1,2-(n-propyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl_2 (8.47 g) over 10 minutes. This solution may need to be gently heated to 45°C for a brief period (5 minutes) to fully dissolve the molecule. The vessel containing the molecule was rinsed with toluene (2 x 10 mL) and added to the reaction mixture. After stirring for 2 hours (200 rpm) at ambient temperature the slurry was filtered, washed with pentane (2 x 200 mL) and dried *in vacuo* to less than 1.5 wt% residual volatiles. The solid catalyst was isolated and stored under nitrogen until further use.

Type 2 Polymerization Catalysts (Inventive: with catalyst modifier present):

a) 1.5 wt% Atmer-163. To a pentane (400 mL) slurry of the catalyst prepared as above (100.17 g of Catalyst Type 1) was added neat Atmer-163 (1.55 g). The slurry was stirred with an overhead stirrer assembly (200 rpm) for 30 minutes at ambient temperature at which point volatiles were removed *in vacuo* while heating to 30°C. The resultant catalyst was dried to less than 1.5 wt% residual volatiles, isolated and stored under nitrogen until further use. b) 1.5 wt% Aromostat-1800. To a slurry of dehydrated silica (58.54 g) in toluene (240 mL) was added a 10 wt% MAO solution (161.89 g of 4.5 wt % Al in toluene) over 35 minutes. The vessel containing the MAO was rinsed with toluene (2 x 25 mL) and added to the reaction mixture. The

resultant slurry was stirred with an overhead stirrer assembly (200 rpm) for 2 hours at ambient temperature. To this slurry was added a toluene (35 mL) solution of (1,2-(n-propyl)(C_6F_5)Cp)Ti(N=P(t-Bu)$_3$)Cl_2 (0.91 g) over 10 minutes. This solution may need to be gently heated to 45°C for a brief period (5 minutes) to fully dissolve the molecule. The vessel containing the molecule was rinsed with toluene (2 x 10 mL) and added to the reaction mixture. After stirring for 2 hours (200 rpm) at ambient temperature a toluene (20 mL) solution of Armostat-1800 (1.37 g) was added to the slurry which was further stirred for 30 minutes. The slurry was decanted, stirred with pentane (100 mL) for 30 minutes and then decanted once again. This step was repeated once more before the catalyst was dried *in vacuo* to less than 1.5 wt% residual volatiles. The solid catalyst was isolated and stored under nitrogen until further use. c) 2.5 wt% Aromostat-1800. A polymerization catalyst containing 2.5 wt% of Armostat-1800 was made similarly to b) above except that the relative amount of Armostat-1800 added was increased to give 2.5 weight per cent of catalyst modifier based on the combined weight of the phosphinimine catalyst, the support and the cocatalyst. d) 3.5 wt% Aromostat-1800. A polymerization catalyst containing 3.5 wt% of Armostat-1800 was made similarly to b) above except that the relative amount of Armostat-1800 added was increased to give 3.5 weight per cent of catalyst modifier based on the combined weight of the phosphinimine catalyst, the support and the cocatalyst.

General polymerization conditions

Continuous ethylene/1-hexene gas phase copolymerization experiments were conducted in a 56.4 litre technical scale reactor (TSR) in continuous gas phase operation (for an example of a TSR reactor set up see Eur. Pat. Appl. No. 659,773A1). Ethylene polymerizations were run at 80°C with a total operating

pressure of 300 pounds per square inch gauge (psig). Gas phase compositions for ethylene, 1-hexene and hydrogen were controlled via closed-loop process control to values of 35-51, 0.5-1.7 and 0.018-0.042 mole percent, respectively. Nitrogen constituted the remainder of the gas phase mixture (approximately 49 mole %). Typical production rate for these conditions was 2.0 to 3.0 kg of polyethylene per hour. Triethylaluminum (TEAL) was fed to the reactor continuously, as a 0.25 wt% solution in hexane (solution fed at about 10 mL/hr) in order to scavenge impurities. The residence time in the reactor is held at 1.5-3.0 hr, with a production rate range from 1.5-2.7 kg/hr.

The catalyst metering device used for administering catalyst to the reactor is equipped with a static probe that measures electrostatic charge carried by the solid material passing through a monitored tube leading catalyst to the reactor.

Polymer Analysis

Melt index, I_2, in g/10 min was determined on a Tinius Olsen Plastomer (Model MP993) in accordance with ASTM D1238 condition F at 190° C with a 2.16 kilogram weight. Melt index, I_{10}, was determined in accordance with ASTM D1238 condition F at 190° C with a 10 kilogram weight. High load melt index, I_{21}, in g/10 min was determined in accordance with ASTM D1238 condition E at 190° C with a 21.6 kilogram weight.

Polymer density was determined in grams per cubic centimeter (g/cc) according to ASTM D1928.

Molecular weight information (M_w, M_n and M_z) and molecular weight distribution (M_w/M_n) were analyzed by gel permeation chromatography (GPC), using an instrument sold under the trade name "Waters 150c", with 1,2,4-trichlorobenzene as the mobile phase at 140° C. The samples were prepared by dissolving the

polymer in this solvent and were run without filtration. Molecular weights are expressed as polyethylene equivalents with a relative standard deviation of 2.9% for the number average molecular weight ("Mn") and 5.0% for the weight average molecular weight ("Mw").

The peak melting point (T_m) and percent of crystallinity of the polymers were determined by using a TA Instrument DSC Q1000 Thermal Analyser at 10°C/min. In a DSC measurement, a heating-cooling-heating cycle from room temperature to 200°C or vice versa was applied to the polymers to minimize the thermo-mechanical history associated with them. The melting point and percent of crystallinity were determined by the primary peak temperature and the total area under the DSC curve respectively from the second heating data. The peak melting temperature T_m is the higher temperature peak, when two peaks are presented in a bimodal DSC profile (typically also having the greatest peak height).

A compression molded film of 0.0035 inches was extracted at 50°C in hexane for 2 hours. The sample was re-weighed and the extractable content was determined from the relative change in sample weight according to ASTM D5227.

The branch frequency of copolymer samples (i.e. the short chain branching, SCB per 1000 carbons) and the C_6 comonomer content (in wt%) was determined by Fourier Transform Infrared Spectroscopy (FTIR) as per the ASTM D6645-01 method. A Thermo-Nicolet 750 Magna-IR Spectrophotometer equipped with OMNIC version 7.2a software was used for the measurements.

The determination of branch frequency as a function of molecular weight (and hence the comonomer distribution profile) was carried out using high temperature Gel Permeation Chromatography (GPC) and FT-IR of the eluent. Polyethylene

standards with a known branch content, polystyrene and hydrocarbons with a known molecular weight were used for calibration.

To determine CDBI, a solubility distribution curve is first generated for the copolymer. This is accomplished using data acquired from the TREF technique. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a cumulative distribution curve of weight fraction versus comonomer content, from which the CDBI is determined by establishing the weight percentage of a copolymer sample that has a comonomer content within 50% of the median comonomer content on each side of the median. The weight percentage of a higher density fraction, (i.e. the wt% eluting from 90-105°C), is determined by calculating the area under the TREF curve at an elution temperature of from 90 to 105°C. The weight percent of copolymer eluting below 40°C can be similarly determined. For the purpose of simplifying the correlation of composition with elution temperature, all fractions are assumed to have a Mn≧15,000, where Mn is the number average molecular weight of the fraction. Any low molecular weight fractions present generally represent a trivial portion of the polymer. The remainder of this description maintains this convention of assuming all fractions have Mn≧15,000 in the CDBI measurement.

Temperature rising elution fractionation (TREF) method. Polymer samples (50 to 150 mg) were introduced into the reactor vessel of a crystallization-TREF unit (Polymer ChAR^{TM}). The reactor vessel was filled with 20 to 40 ml 1,2,4-trichlorobenzene (TCB), and heated to the desired dissolution temperature (e.g. 150 °C) for 1 to 3 hours. The solution (0.5 to 1.5 ml) was then loaded into the TREF column filled with stainless steel beads. After equilibration at a given stabilization temperature (e.g. 110 °C) for 30 to 45 minutes, the polymer solution was allowed to

crystallize with a temperature drop from the stabilization temperature to 30°C (0.1 or 0.2 °C/minute). After equilibrating at 30°C for 30 minutes, the crystallized sample was eluted with TCB (0.5 or 0.75 mL/minute) with a temperature ramp from 30°C to the stabilization temperature (0.25 or 1.0 °C/minute). The TREF column was cleaned at the end of the run for 30 minutes at the dissolution temperature. The data were processed using Polymer ChAR software, Excel spreadsheet and TREF software developed in-house.

The TREF procedure described above is well known to persons skilled in the art and can be used to determine: the overall TREF profile, CDBI, copolymer wt% below 40°C, and copolymer wt% from 90°C to 105°C .

Gel Count Procedure

An in-lab OCS gel measurement system, which consists of an OCS gel camera, FSA 100 film scanning unit, image analysis software, cast line extruder and chill roll windup setup, is used to determine the amount of gels in a 1.0 to 2.0 mil cast film. For a gel count measurement, a polymer sample is added into a 20 mm extruder with a mixing screw of 3:1 or 4:1 compression ratio and run at 60 rpm. The haul-off speed and chill roll temperature of the cast film line are set at 8.0 m/min and 23 to 30°C respectively. The pictures of cast film are taken by an OCS camera continuously and the film scanning unit with image analysis software is used to monitor the gel data in the pictures. The gel counts in a cast film are defined as the total area of defects per total area measured and reported as a total ppm value.

Polymerization Results

Examples 1, 3, 5, 6 and 13 (comparative baseline runs). The Type 1 Catalyst (prepared as described above) was placed under a N2 blanket and using a dry catalyst feeder, a small shot of supported catalyst was continuously added to a

technical scale reactor via a feeding tube. Equilibrium polymerization conditions were established after a period of 4 residence times. Once equilibrium conditions were established, the static level in the reactor was measured over 6 hrs using a static probe (Correflow Electrostatic Monitor 3410™ available from Progression). The static probe was located within the polymerization reactor. The temperature in the reactor over this time was also determined. Several similar runs were carried out at different times to establish baseline run conditions prior to running an inventive example (see "baseline" Run Nos. 1, 3, 5, 6 and 13 of Table 1). Static of the solid catalyst entering the reactor was also measured within the catalyst metering area over the 6 hr period. Relevant data for these examples are provided in Table 1.

Examples 2, 4, 7-12 (catalyst modifier added to catalyst). In each polymerization run, a Type 2 polymerization catalyst (each of the Type 2 Catalysts 2a-2d, are prepared as described above using various amounts of a catalyst modifier) was placed under a N2 blanket and using a dry catalyst feeder, a small shot of supported catalyst was continuously added to a technical scale reactor via a feeding tube. Equilibrium polymerization conditions were established after a period of 4 residence times. Once equilibrium conditions were established, the static level in the reactor was measured over 6 hrs using a static probe (Correflow Electrostatic Monitor 3410 available from Progression). The static probe was located within the polymerization reactor. The temperature in the reactor was also determined over this time. Polymerization runs using Type 2 catalysts are inventive runs (see "inventive" polymerization Run Nos. 2, 4, 7-12 in Table 1) and were carried out soon after establishing appropriate baseline conditions. Static of the solid catalyst entering the reactor was also measured within the catalyst metering area over the 6

hr period. An examination of the polymer product obtained during each of these runs revealed a free flowing powder without significant chunks or strings. Relevant data for these examples are provided in Table 1.

Examples 14 and 15 (catalyst modifier added to the reactor). To provide a comparison between adding catalyst modifier directly to the reactor and including a catalyst modifier in the catalyst formulation, polymerization runs were conducted in which the catalyst modifier was added to the reactor directly, instead of including the catalyst modifier in the polymerization catalyst (see "inventive" Run Nos. 14 and 15). These examples were conducted in a manner analogous to Example 1, except that once equilibrium polymerization conditions were established, a catalyst modifier was fed to the reactor. The catalyst modifier was Atmer-163 which was diluted in hexanes to give a 1% by weight mixture and added via a manifold, into the reactor. In Example 14, 25 ppm of Atmer-163 (per mass of polymer produced) was fed to the reactor. Once steady state was achieved, the reaction was held constant for another 3-4 residence times, and then the static level in the reactor was measured over 6 hours. Temperature in the reactor was measured, and the static of the catalyst entering the reactor was measured within the catalyst metering area over the 6 hr period. In Example 15, the level of Atmer-163 fed to the reactor was increased from 25 ppm to 100 ppm (based on the weight of the polymer produced) and then the static level was measured over 6 hours. Temperature in the reactor was measured and the static of the catalyst entering the reactor was measured within the catalyst metering area over the 6 hr period. An examination of the polymer product obtained during Atmer-163 addition revealed a free flowing powder without significant chunks or strings. Relevant data for these examples are provided in Table 1.

TABLE 1

Static Level, Catalyst Productivity and Reactor Temperature Range

Examples (Poly. Run No.)	Catalyst Modifier in Catalyst	Catalyst Modifier fed to Reactor	Productivity (g poly/g cat)	Catalyst Static Level[1]	Reactor Static Level[2]	Temp. Standard Deviation[3]
1 (baseline)	none	none	3209	0.045	0.71	1.2
2 (inventive)	1.5 wt% Atmer-163	none	4423	0.020	0.39	0.4
3 (baseline)	none	none	4900	0.031	0.63	0.7
4 (inventive)	1.5 wt% Armostat-1800	none	5346	0.016	0.86[4]	0.5
5 (baseline)	none	none	3909	0.041	0.43	0.8
6 (baseline)	none	none	4043	0.029	0.42	0.7
7 (inventive)	1.5 wt% Armostat-1800	none	4238	0.022	0.26	0.4
8 (inventive)	2.5 wt% Armostat-1800	none	6842	0.023	0.87[5]	0.3
9 (inventive)	2.5 wt% Armostat-1800	none	5418	0.023	0.32	0.3
10 (inventive)	1.5 wt% Armostat-1800	none	5328	0.013	0.26	0.5
11 (inventive)	3.5 wt% Armostat-1800	none	4751	0.019	0.34	0.3
12 (inventive)	3.5 wt% Armostat-1800	none	5000	0.016	0.58[6]	0.6
13 (baseline)	None	none	3955	0.019	0.47	--

14 (inventive)	None	25 ppm Atmer-163	3653	0.026	0.31	--
15 (inventive)	None	100 ppm Atmer-163	276	0.027	0.29	--

Note 1: The static level of the catalyst entering the reactor was measured by using a Correstat 3410 static probe over a 6 hr period. To obtain this value, a static signal, in nanoamps, is recorded each second in the catalyst metering tube. These signals are transformed into positive values by taking the absolute value of each number. The sum of the absolute values is divided by the number of seconds used to calculate the sum; this number is reported in Table 1. Note 2: The static level of solids in the reactor was measured with a Correstat 3410 static probe over a 6 hr period. To obtain this value, a static signal, in nanoamps, is recorded each second at the reactor wall. These signals are transformed into positive values by taking the absolute value of each number. The sum of the absolute values is divided by the number of seconds used to calculate the sum; this number is reported in Table 1. Note 3: The standard deviation in temperature. Standard deviation of the reactor temperature is a way to quantify how much the reactor temperature fluctuates from the mean temperature or control temperature. A smaller standard deviation means smaller temperature fluctuations around the control temperature. A larger standard deviation means larger temperature fluctuations around the control temperature. In the data set generated for the patent, the standard deviation was calculated over 10 hours of steady state operation. Note 4: This run had a higher than expected reactor static reading for unknown reasons. We note however, that the catalyst static level and the size of the temperature excursion are both low relative to the baseline case (Run. No. 3). Note 5: An unexpected increase in static suddenly occurred during this run. Examination of the polymer showed a small amount of roped material which may have artificially increased the overall static measurement within the last 6hrs of this run. An examination of the static levels prior to the static spike was consistent with an overall static measurement of 0.49 (i.e. over the previous 6hrs). Note 6: An ethylene pressure supply problem created pressure swings in the reactor which may have impacted the reactor static measurement.

The data in Table 1 show that the inclusion of a catalyst modifier in the polymerization catalyst can improve catalyst productivity, and that to improve productivity, the preferred amounts of catalyst modifier added are somewhere from about 0.5 wt% to about 4.0 wt% based on the weight of the polymerization catalyst.

The data provided in Table 1 further show that inclusion of a catalyst modifier within the polymerization catalyst or feeding a catalyst modifier directly to the reactor reduced at least one of: reactor static level, catalyst static level, and reactor temperature excursions. With the exception of Run No. 8 (in which a small amount of polymer rope was formed; see Note 5) visual examination of all polymer products obtained using a Type 2 Catalyst revealed products which were free flowing powders without significant chunks or strings. Similarly, visual examination of the polymer product obtained when a catalyst modifier was added directly to the reactor revealed a free flowing powdered product. Hence, the data show that reactor continuity and operability improves when a catalyst modifier is included in the polymerization catalyst formulation or when a catalyst modifier is fed directly to the polymerization reactor.

In addition to improvements in reactor operability, we have found that changing the amount of catalyst modifier in the polymerization catalyst or changing the amount of catalyst modifier fed to the reactor dramatically affects copolymer product architecture while not significantly changing the polymer density or melt index, I_2. The polymer properties of copolymers isolated from polymerization Run Nos. 2, 4, 6, 9, 11 and 14, are provided below in Table 2. Figure 1 shows the comonomer distribution profile as obtained by GPC-FTIR on a copolymer obtained from a typical baseline run (e.g. Run No. 6). Figure 2 shows a TREF profile for a copolymer obtained from a typical baseline run (e.g. Run No. 6).

TABLE 2

Polymer Properties

Poly. Run No.	6	14	2	4	9	11
Catalyst Modifier in Catalyst	none	None	1.5 wt% Atmer-163	1.5 wt% Armostat-1800	2.5 wt% Armostat-1800	3.5 wt% Armostat-1800
Catalyst Modifier fed to Reactor	none	25 ppm Atmer-163	none	None	none	none
Density (g/cc)	0.9182	0.9174	0.9189	0.9180	0.9186	0.9185
I_2 (g/10 min)	1.01	1.03	0.89	1.03	0.90	0.93
I_{10}/I_2	5.78	5.63	5.76	5.64	5.64	5.66
I_{21}/I_2	16.3	15.9	16.7	15.8	14.1	16.1
CDBI	**50.2**	**58.2**	**55.2**	**57.9**	**61.4**	**58.1**
TREF (90-105°C, wt%)	**20.4**	**15.3**	**20.9**	**16.7**	**15.4**	**17.0**
Mn	52879	55077	50825	47455	53940	57167
Mw	103750	104231	109275	100157	106495	106771
Mz	177076	179401	205446	164387	177080	174086
Mw/Mn	1.96	1.89	2.15	2.11	1.97	1.87
scb/1000 C's	10.4	10.9	9.6	10.1	10.0	10.3
mole% of C6	2.1	2.2	1.9	2.0	2.0	2.1
wt% of C6	6.00	6.20	5.5	5.80	5.70	5.90
Comonomer	hexene	hexane	hexane	hexane	hexene	hexene
Comonomer Profile (GPC-FTIR)	**normal**	**flat**	**reversed**	**reversed**	**reversed**	**partially reversed**
Peak Melting Temperature (°C)	118.5	117.0	119.0	117.6	117.3	117.3
% Crystallinity	44.2	44.5	45.3	47.4	44.5	44.6
Hexane Extractables	0.21	0.19	0.22	0.22	0.27	0.26

(%)						

The data in Table 2 show that the "composition distribution" of the resulting copolymers changes relative to the amount of catalyst modifier present in the polymerization catalyst or added to the reactor. Indices which characterize changes in "composition distribution" of the ethylene copolymer include changes to one or more of the following: A) the composition distribution breadth index (CDBI) of the ethylene copolymer as measured using temperature rising elution fractionation (TREF) methods; B) the weight percent of a higher temperature eluting material (i.e. from 90°C to 105°C) observed in TREF profile obtained for the ethylene copolymer; and C) the comonomer distribution profile of the ethylene copolymer as measured by gel permeation chromatography with Fourier transform infra-red detection (GPC-FTIR).

Polymerization Run No. 2 employed the Type 2a catalyst (1.5 wt% of Atmer-163 in the catalyst). The polymerization results and selected polymer characterization data are provided in Tables 1 and 2. The GPC-FTIR and TREF data are provided in Figures 3 and 4 for the product obtained from Run No. 2. When taking the copolymer produced in Run No. 6 as a benchmark, a comparison of the polymer data in Table 2 (compare Run No. 6 with Run No. 2) and a comparison between Figures 1 and 3, shows that increasing the amount of Atmer-163 present in the polymerization catalyst from 0 to 1.5 wt% caused an increase in the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights as measured by GPC-FTIR. In fact, the comonomer distribution profile changed from normal to reversed. Also evident from the data in Table 2 and from a comparison between Figures 2 and 4 is that an increase in the

amount of Atmer-163 present in the polymerization catalyst from 0 to 1.5 wt% caused the comonomer distribution breath index (CDBI) to increase from 50.2% to 55.2% (see Table 2).

Polymerization Run Nos. 4, 7, and 10 employed the Type 2b catalyst (1.5 wt% of Armostat-1800 in the catalyst). The polymerization results and selected polymer characterization data are provided in Tables 1 and 2. The GPC-FTIR and TREF data are provided in Figures 5 and 6 for the product obtained from Run No. 4. When taking the copolymer produced in Run No. 6 as a benchmark, a comparison of the polymer data in Table 2 (compare Run No. 6 with Run No. 4) and a comparison between Figures 1 and 5, shows that increasing the amount of Armostat-1800 present in the polymerization catalyst from 0 to 1.5 wt% caused an increase in the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights as measured by GPC-FTIR. In fact, the comonomer distribution profile changed from normal to slightly reversed. Also evident from the data in Table 2 and from a comparison between Figures 2 and 6, is that increasing the amount of Armostat-1800 present in the polymerization catalyst from 0 to 1.5 wt% caused a decrease in the weight percent of an ethylene copolymer which elutes at from 90°C to 105°C in a TREF analysis. The amount of copolymer eluting at from 90°C to 105°C decreased from 20.4 wt% to 16.7 wt%. Another consequence of increasing the amount of Armostat-1800 present in the polymerization catalyst by 1.5 wt% was that the comonomer distribution breath index (CDBI) increased from 50.2% to 57.9% (see Table 2).

Polymerization Run Nos. 8 and 9 employed the Type 2c catalyst (2.5 wt% of Armostat-1800 in the catalyst). The polymerization results and selected polymer characterization data are provided in Tables 1 and 2. The GPC-FTIR is provided in

Figure 7 for the product obtained from Run No. 9. When taking the copolymer produced in Run No. 6 as a benchmark, a comparison of the polymer data in Table 2 (compare Run No. 6 with Run No. 9) and a comparison between Figures 1 and 7, shows that increasing the amount of Armostat-1800 present in the polymerization catalyst from 0 to 2.5 wt% caused an increase in the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights as measured by GPC-FTIR. In fact, the comonomer distribution profile changed from normal to reversed. Also evident from the data in Table 2, is that increasing the amount of Armostat-1800 present in the polymerization catalyst from 0 to 2.5 wt% caused a decrease in the weight percent of an ethylene copolymer which elutes at from 90°C to 105°C in a TREF analysis. The amount of copolymer eluting at from 90°C to 105°C decreased from 20.4 wt% to 15.4 wt%. Another consequence of increasing the amount of Armostat-1800 present in the polymerization catalyst by 2.5 wt% was that the comonomer distribution breath index (CDBI) increased from 50.2% to 61.4% (see Table 2).

Polymerization Run Nos. 11 and 12 employed the Type 2d catalyst (3.5 wt% of Armostat-1800 in the catalyst). The polymerization results and selected polymer characterization data are provided in Tables 1 and 2. The GPC-FTIR is provided in Figure 8 for the product obtained from Run No. 11. When taking the copolymer produced in Run No. 6 as a benchmark, a comparison of the polymer data in Table 2 (compare Run No. 6 with Run No. 11) and a comparison between Figures 1 and 8, shows that increasing the amount of Armostat-1800 present in the polymerization catalyst from 0 to 3.5 wt% caused an increase in the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights as measured by GPC-FTIR. In fact, the comonomer distribution profile changed from

normal to partially reversed. Also evident from the data in Table 2, is that increasing the amount of Armostat-1800 present in the polymerization catalyst from 0 to 3.5 wt% caused a decrease in the weight percent of an ethylene copolymer which elutes at from 90°C to 105°C in a TREF analysis. The amount of copolymer eluting at from 90°C to 105°C decreased from 20.4 wt% to 17.0 wt%. Another consequence of increasing the amount of Armostat-1800 present in the polymerization catalyst by 3.5 wt% was that the comonomer distribution breath index (CDBI) increased from 50.2% to 58.1% (see Table 2).

Polymerization Run Nos. 14 and 15 employed the Type 1 catalyst and the catalyst modifier was added directly to the reactor. The polymerization results and selected polymer characterization data are provided in Tables 1 and 2 respectively. The GPC-FTIR and TREF data are provided in Figures 9 and 10 respectively for the product obtained from Run No. 14. When taking the copolymer produced in Run No. 6 as a benchmark, a comparison of the polymer data in Table 2 (compare Run No. 6 with Run No. 14) and a comparison between Figures 1 and 9, shows that increasing the amount of Atmer-163 fed to a polymerization reactor from 0 to 25 ppm caused an increase in the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights as measured by GPC-FTIR. In fact, the comonomer distribution profile changed from normal to flat. Also evident from the data in Table 2, is that increasing the amount of Atmer-163 fed to the polymerization reactor from 0 to 25 ppm caused a decrease in the weight percent of an ethylene copolymer which elutes at from 90°C to 105°C in a TREF analysis. The amount of copolymer eluting at from 90°C to 105°C decreased from 20.4 wt% to 15.3 wt%. Another consequence of increasing the amount of Atmer-163 fed directly

to the polymerization reactor by 25 ppm was that the comonomer distribution breath index (CDBI) increased from 50.2% to 58.2% (see Table 2).

The above examples demonstrate that that inclusion of the catalyst modifier in the polymerization catalyst or addition of the catalyst modifier to the reactor improves short chain branching (i.e. comonomer) homogeneity. In fact the CDBI was increased by more than 5% in each case and more than 10% for the copolymer obtained in Run No. 9. The comonomer distribution profile is also changed. When a Type 2 Catalyst is employed, or when the catalyst modifier is added to the reactor, the amount of comonomer incorporation at higher molecular weights relative to lower molecular weights (as measured by GPC-FTIR) increased (compared to the comonomer incorporation at higher molecular weights relative to lower molecular weights when a Type 1 Catalyst is used or when no catalyst modifier is added to the reactor). Increasing the amount of comonomer incorporation at higher molecular weights may improve many polymer end use properties such as dart impact, puncture resistance, optical property, hot tack or seal performance.

A comparison of the copolymer products obtained from polymerization Run Nos. 4, 9 and 11, further shows that a small change in the amount of catalyst modifier included in the polymerization catalyst (e.g. a change of 1 wt%) provides marked changes in the CDBI, the wt% of copolymer eluting at from 90 to 100°C in a TREF, and the comonomer distribution profile.

Finally we note that inclusion of a catalyst modifier in the polymerization catalyst or addition of a catalyst modifier to the reactor, improved the gel properties of cast film made from the copolymer products obtained. The gel properties of copolymers isolated from selected polymerization runs are provided below in Table 3.

TABLE 3

Gels in Cast Film

Poly. Run No.	Catalyst Modifier in Catalyst	Catalyst Modifier fed to Reactor	OCS Gel Count (ppm)
5	none	none	83
6	none	none	141
7	1.5 wt% Armostat-1800	none	9
9	2.5 wt% Armostat-1800	none	6
11	3.5 wt% Armostat-1800	none	7
14	none	25 ppm Atmer-163	13

Table 3 shows that use of a Type 1 Catalyst (no catalyst modifier) gives copolymer product which when cast into film has high gels counts (83 and 141 for baseline runs 5 and 6) while use of a Type 2 Catalyst (includes a catalyst modifier) gives copolymer product which has a gel count of below 10 when cast into film. Table 3 also shows that addition of a catalyst modifier directly to the polymerization reactor (e.g. 25 ppm Atmer-163) likewise causes a large drop in the gel count.

From the data provided in the above examples, a person skilled in the art will recognize that small changes in the amount of catalyst modifier present in the polymerization catalyst or added to the polymerization reactor can be used to change the ethylene copolymer architecture, namely the composition distribution as indicated by A) the composition distribution breadth index (CDBI) of the ethylene copolymer as measured using temperature rising elution fractionation (TREF) methods; B) the weight percent of a higher temperature eluting material (i.e. from

90°C to 105°C) observed in TREF profile obtained for the ethylene copolymer; and

C) the comonomer distribution profile in the ethylene copolymer as measured by gel permeation chromatography with Fourier transform infra-red detection (GPC-FTIR).

Hence, the architecture of copolymers made with the present catalysts, which minimally contain a phosphinimine catalyst, an inert support and a cocatalyst, can be tuned by altering the amount of catalyst modifier added to a reactor or present in the catalyst.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for altering the composition distribution of an ethylene copolymer, the method comprising:

introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising a phosphinimine catalyst, an inert support, and a cocatalyst;

feeding from 0 to 100 ppm of a catalyst modifier into the reactor (based on the weight of copolymer produced), the catalyst modifier comprising a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and

polymerizing ethylene and an alpha-olefin in the reactor to give the ethylene copolymer;

wherein the composition distribution of the ethylene copolymer is altered by changing the amount of the catalyst modifier fed to the reactor by at least 5 ppm (based on the weight of copolymer produced).

2. The method of claim 1 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N((CH_2)_nOH)((CH_2)_mOH)$ where R^1 is a hydrocarbyl group having anywhere from 5 to 30 carbon atoms, and n and m are integers from 1 to 20.

3. The method of claim 1 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N((CH_2)_xOH)_2$ where R^1 is a hydrocarbyl group having anywhere from 6 to 30 carbon atoms, and x is independently an integer from 1-20.

4. The method of claim 1 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N((CH_2)_xOH)_2$ where R^1 is a hydrocarbyl group having anywhere from 6 to 30 carbon atoms, and x is 2 or 3.

5. The method of claim 1 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a hydrocarbyl group having anywhere from 8 to 22 carbon atoms.

6. The method of claim 1 wherein the catalyst modifier comprises a compound represented by the formula: $C_{18}H_{37}N(CH_2CH_2OH)_2$.

7. The method of claim 1 wherein the catalyst modifier comprises compounds represented by the formulas: $C_{13}H_{27}N(CH_2CH_2OH)_2$ and $C_{15}H_{31}N(CH_2CH_2OH)_2$.

8. The method of claim 1 wherein the catalyst modifier is a mixture of compounds represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a hydrocarbyl group having anywhere from 8 to 18 carbon atoms.

9. The method of claim 1 wherein the phosphinimine catalyst has the formula: $(L)(PI)MX_2$, where M is Ti, Zr or Hf; PI is a phosphinimine ligand having the formula

$R_3P=N-$, where R is independently selected from the group consisting of hydrogen, halogen, and C_1-C_{20} hydrocarbyl; L is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl, and substituted fluorenyl; and X is an activatable ligand.

10. The method of claim 1 wherein the phosphinimine catalyst has the formula: $(1,2\text{-}(R^*)(Ar\text{-}F)Cp)Ti(N=P(t\text{-}Bu)_3)X_2$, where R^* is a straight chain alkyl group, Ar-F is a perfluorinated aryl group, a 2,6 fluoro substituted phenyl group or a 2,3,5,6 fluoro substituted phenyl group, and X is an activatable ligand.

11. The method of claim 1 wherein the cocatalyst is selected from the group consisting of ionic activators, hydrocarbyl aluminoxanes and mixtures thereof.

12. The method of claim 1 wherein the inert support is silica.

13. The method of claim 12 wherein the silica support has been treated with a source of $Zr(SO_4)_2$ or ZrO_2.

14. The method of claim 1 wherein ethylene and an alpha-olefin are polymerized in a gas phase fluidized bed reactor.

15. The method of claim 1 wherein from 1 to 50 ppm of the catalyst modifier is fed to the reactor (based on the weight of the copolymer produced).

16. A method for altering the composition distribution of an ethylene copolymer, the method comprising:

introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst; and further including from 0 to 10 weight percent of a catalyst modifier based on the weight of i), ii) and iii) of the polymerization catalyst, the catalyst modifier comprising a compound having the formula $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and

polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer;

wherein the composition distribution of the ethylene copolymer is altered by changing the amount of the catalyst modifier included in the olefin polymerization catalyst by at least 0.25 weight percent (based on the weight of i), ii) and iii) of the polymerization catalyst).

17. The method of claim 16 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N((CH_2)_nOH)((CH_2)_mOH)$ where R^1 is a hydrocarbyl group having anywhere from 5 to 30 carbon atoms, and n and m are integers from 1 to 20.

18. The method of claim 16 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N((CH_2)_xOH)_2$ where R^1 is a hydrocarbyl

group having anywhere from 6 to 30 carbon atoms, and x is independently an integer from 1 to 20.

19. The method of claim 16 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N((CH_2)_xOH)_2$ where R^1 is a hydrocarbyl group having anywhere from 6 to 30 carbon atoms, and x is 2 or 3.

20. The method of claim 16 wherein the catalyst modifier comprises at least one compound represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a hydrocarbyl group having anywhere from 8 to 22 carbon atoms.

21. The method of claim 16 wherein the catalyst modifier comprises a compound represented by the formula: $C_{18}H_{37}N(CH_2CH_2OH)_2$.

22. The method of claim 16 wherein the catalyst modifier comprises compounds represented by the formulas: $C_{13}H_{27}N(CH_2CH_2OH)_2$ and $C_{15}H_{31}N(CH_2CH_2OH)_2$.

23. The method of claim 16 wherein the catalyst modifier is a mixture of compounds represented by the formula: $R^1N(CH_2CH_2OH)_2$ where R^1 is a hydrocarbyl group having anywhere from 8 to 18 carbon atoms.

24. The method of claim 16 wherein the phosphinimine catalyst has the formula: $(L)(PI)MX_2$, where M is Ti, Zr or Hf; PI is a phosphinimine ligand having the formula $R_3P=N-$, where R is independently selected from the group consisting of hydrogen, halogen, and C_1-C_{20} hydrocarbyl; L is a ligand selected from the group consisting of

cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl, and substituted fluorenyl; and X is an activatable ligand.

25. The method of claim 16 wherein the phosphinimine catalyst has the formula: $(1,2\text{-}(R^*)(Ar\text{-}F)Cp)Ti(N{=}P(t\text{-}Bu)_3)X_2$, where R^* is a straight chain alkyl group, Ar-F is a perfluorinated aryl group, a 2,6 fluoro substituted phenyl group or a 2,3,5,6 fluoro substituted phenyl group, and X is an activatable ligand.

26. The method of claim 16 wherein the cocatalyst is selected from the group consisting of ionic activators, hydrocarbyl aluminoxanes and mixtures thereof.

27. The method of claim 16 wherein the inert support is silica.

28. The method of claim 27 wherein the silica support has been treated with a source of $Zr(SO_4)_2$ or ZrO_2.

29. The method of claim 16 wherein ethylene and an alpha-olefin are polymerized in a gas phase fluidized bed reactor.

30. The method of claim 16 wherein the catalyst modifier further included in the polymerization catalyst is present in from 0.25 to 6.0 weight percent, based on the weight of i), ii) and iii) of the polymerization catalyst.

31. A method for altering the composition distribution of an ethylene copolymer, the method comprising:

introducing a polymerization catalyst into a gas phase reactor, the polymerization catalyst comprising i) a phosphinimine catalyst, ii) an inert support, iii) a cocatalyst and further including from 0 to 10 wt% of a catalyst modifier (based on the weight of i), ii) and iii) of the polymerization catalyst);

feeding from 0 to 100 ppm of a catalyst modifier (based on the weight of copolymer produced) into the gas phase reactor; and

polymerizing ethylene and an alpha-olefin in the gas phase reactor to give the ethylene copolymer;

wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor each comprise a compound having the formula: $R^1R^2_xN((CH_2)_nOH)_y$ where R^1 is a hydrocarbyl group having from 5 to 30 carbon atoms, R^2 is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, x is 1 or 0, y is 1 when x is 1, y is 2 when x is 0, each n is independently an integer from 1 to 30 when y is 2, and n is an integer from 1 to 30 when y is 1; and

wherein the composition distribution of the ethylene copolymer is altered by changing at least one of the following:

a) the amount of the catalyst modifier fed into the gas phase reactor by at least 5 ppm (based on the weight of copolymer produced);

b) the amount the catalyst modifier included in the polymerization catalyst by at least 0.5 wt% (based on the weight of i), ii) and iii) of the polymerization catalyst).

32. The method of claim 31 wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor comprise different long chain dialkanolamines.

33. The method of claim 31 wherein the catalyst modifier included in the polymerization catalyst and the catalyst modifier fed into the gas phase reactor comprise the same long chain dialkanolamine.

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FIGURE 1

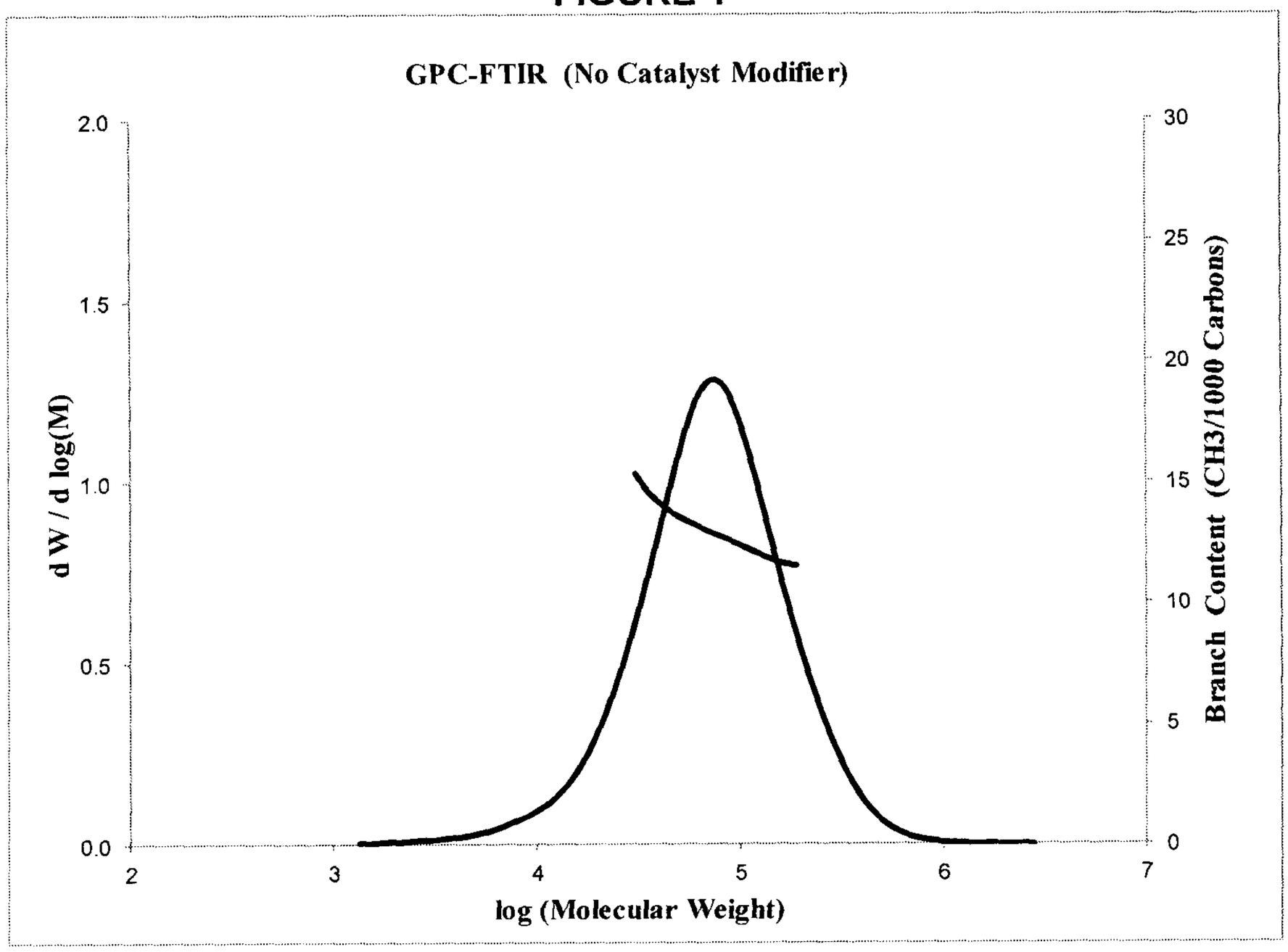
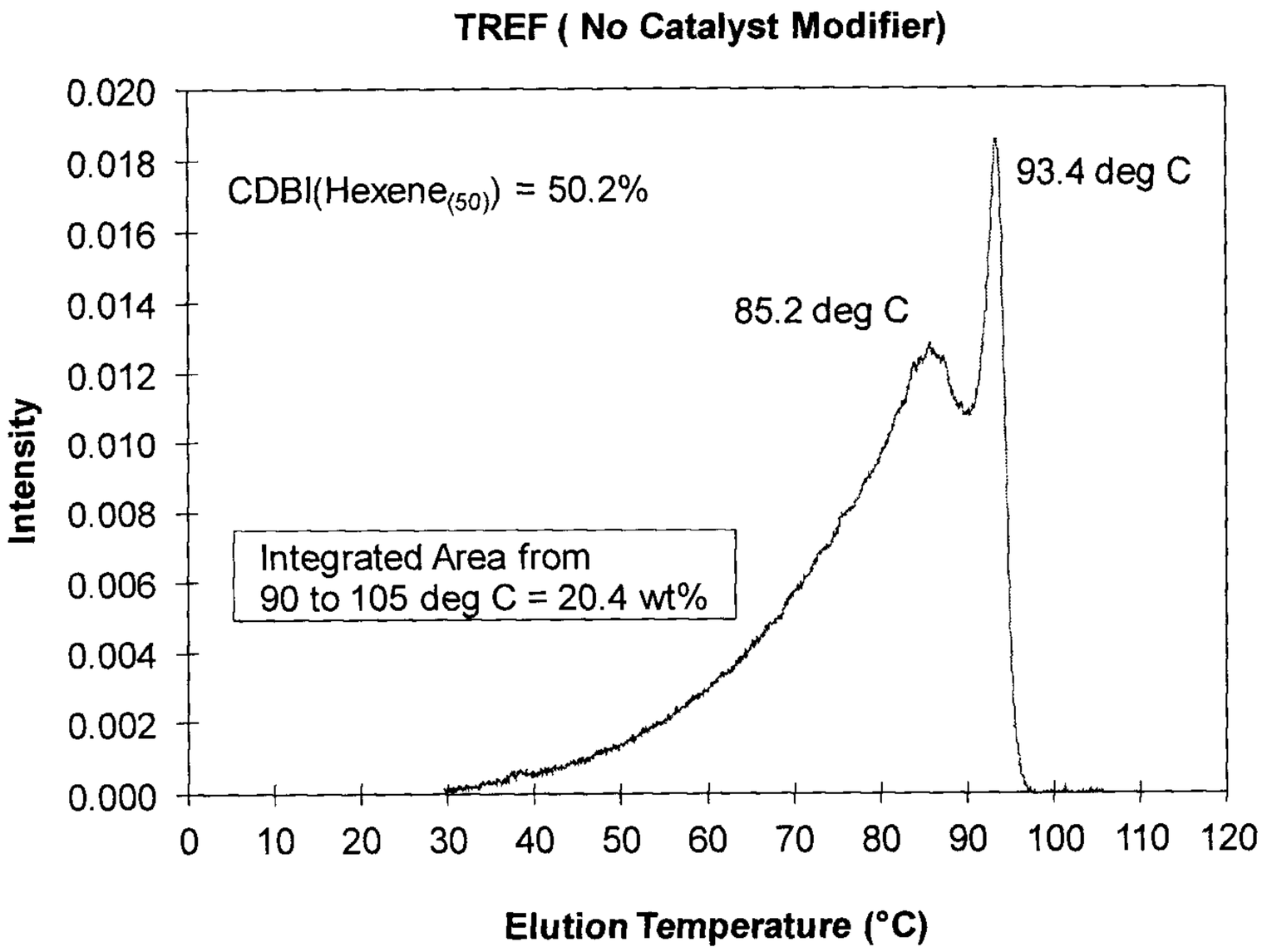


FIGURE 2



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FIGURE 3

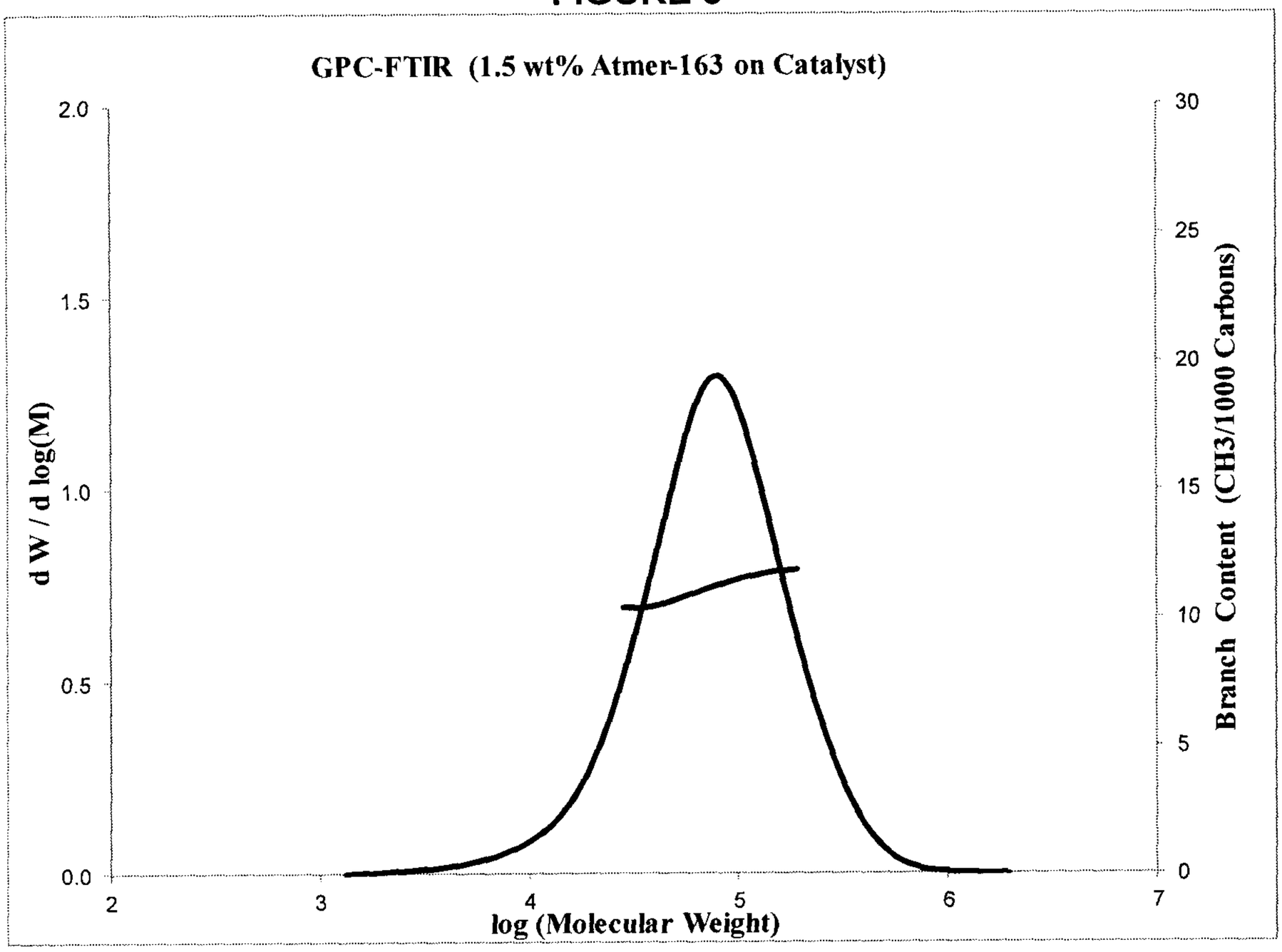
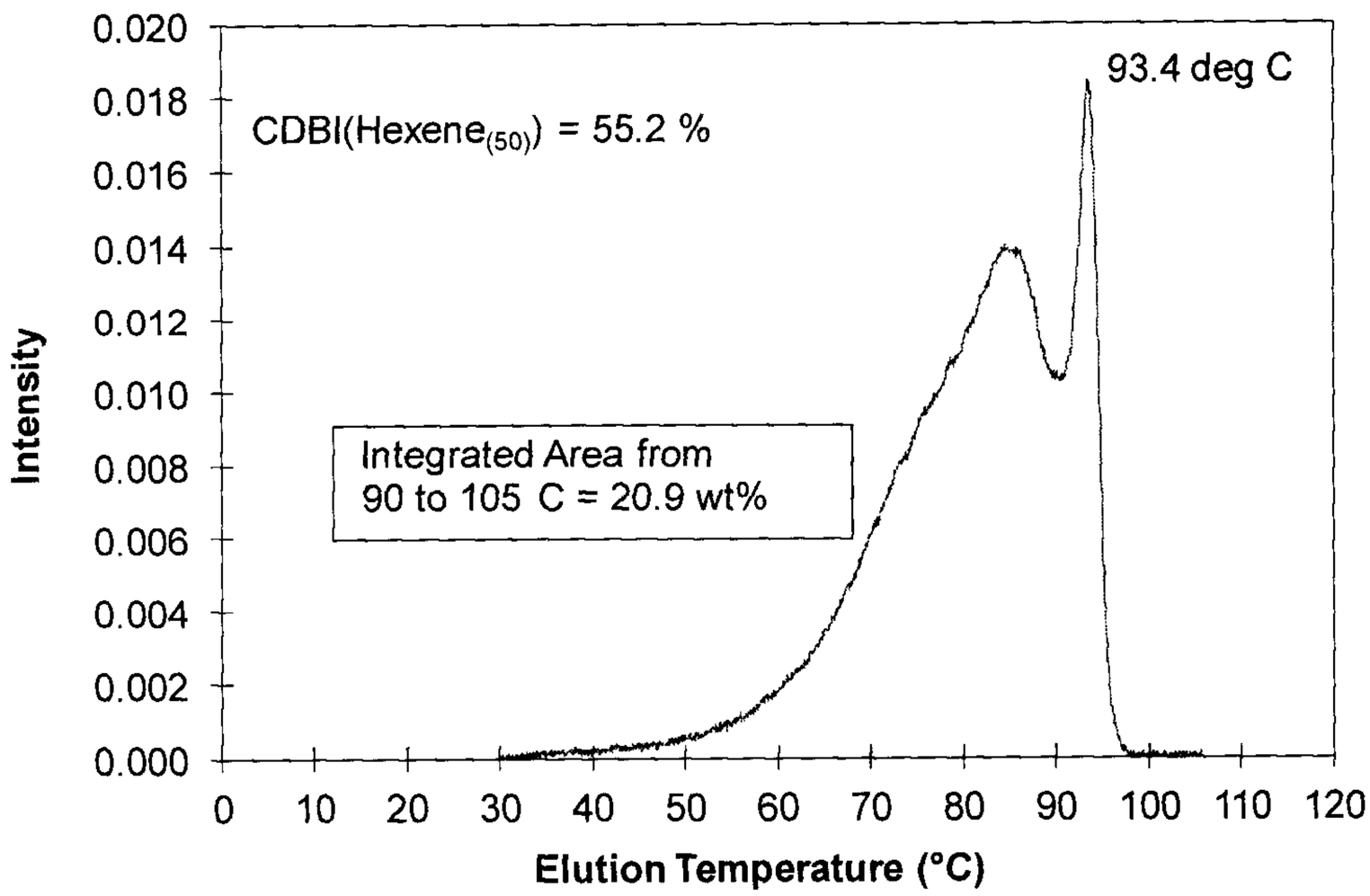


FIGURE 4



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FIGURE 5

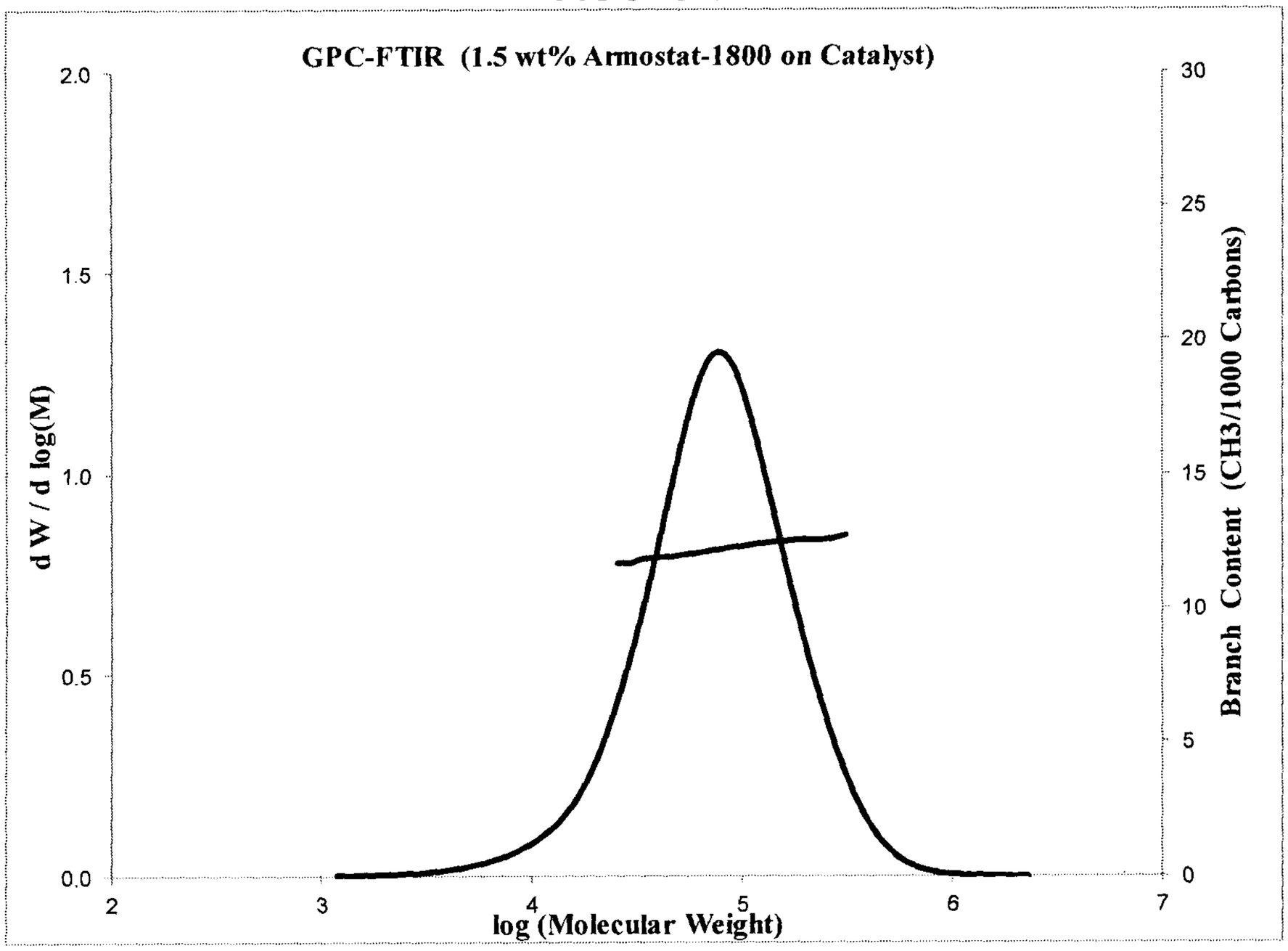
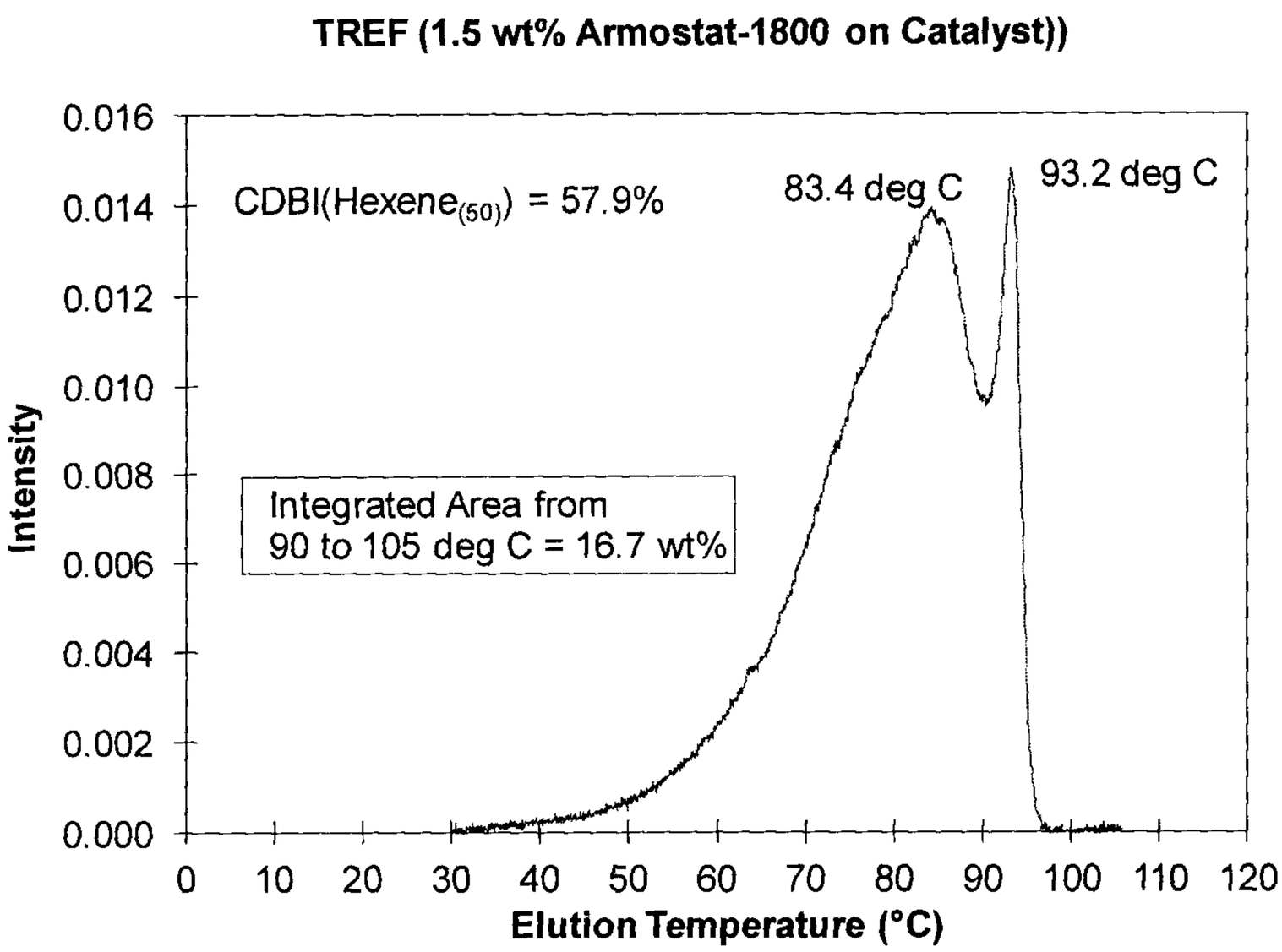


FIGURE 6



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FIGURE 7

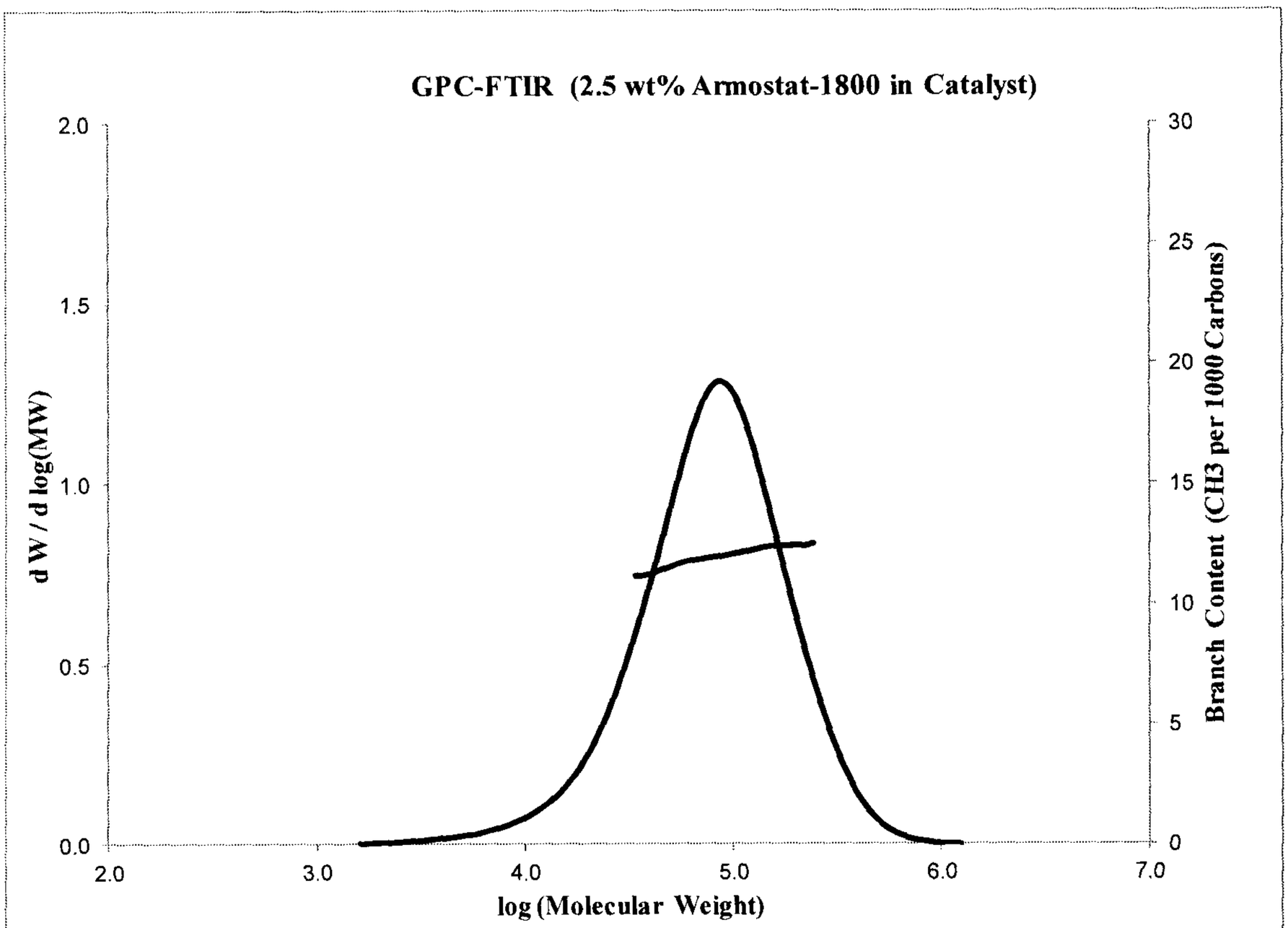
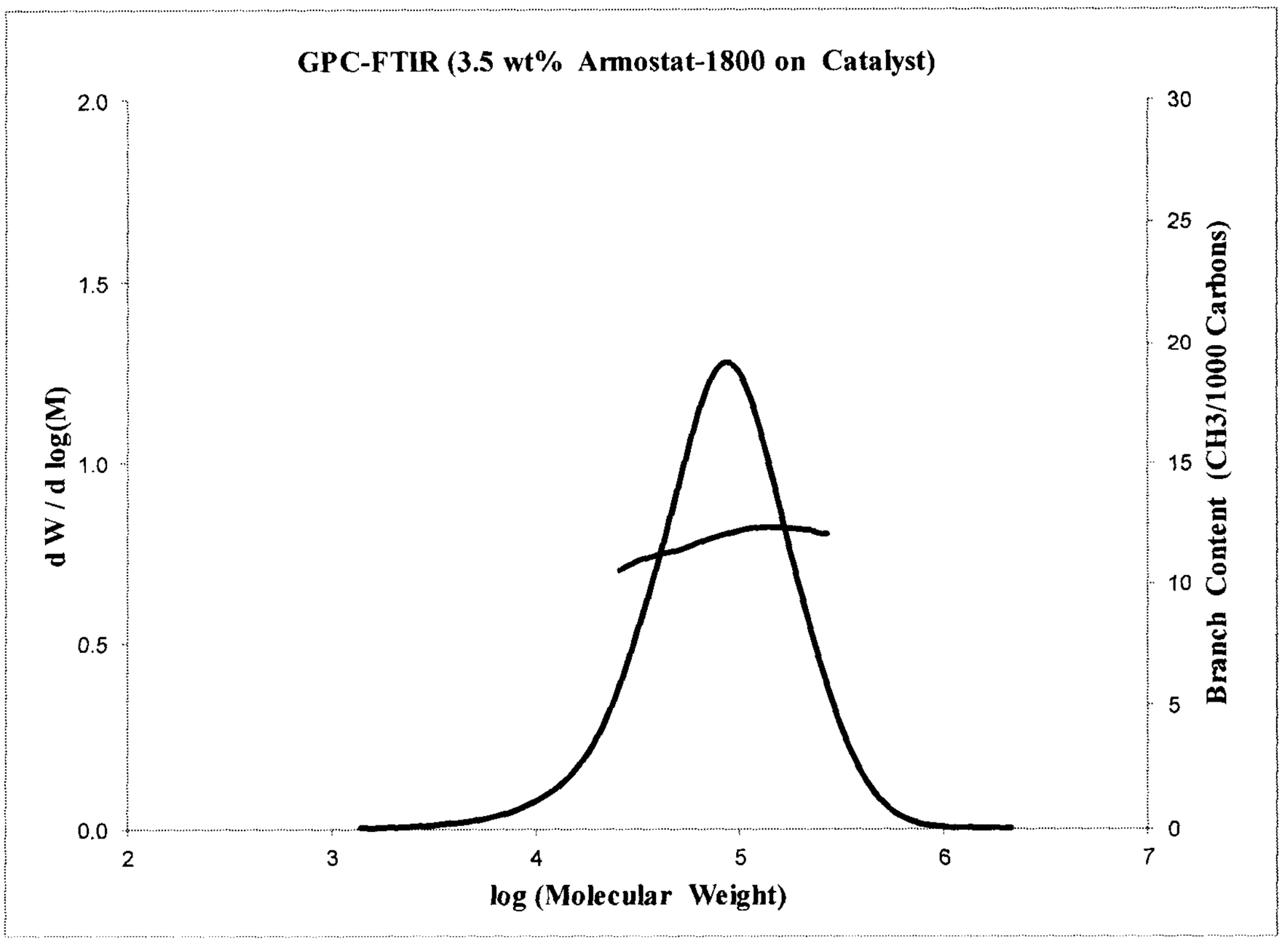


FIGURE 8



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FIGURE 9

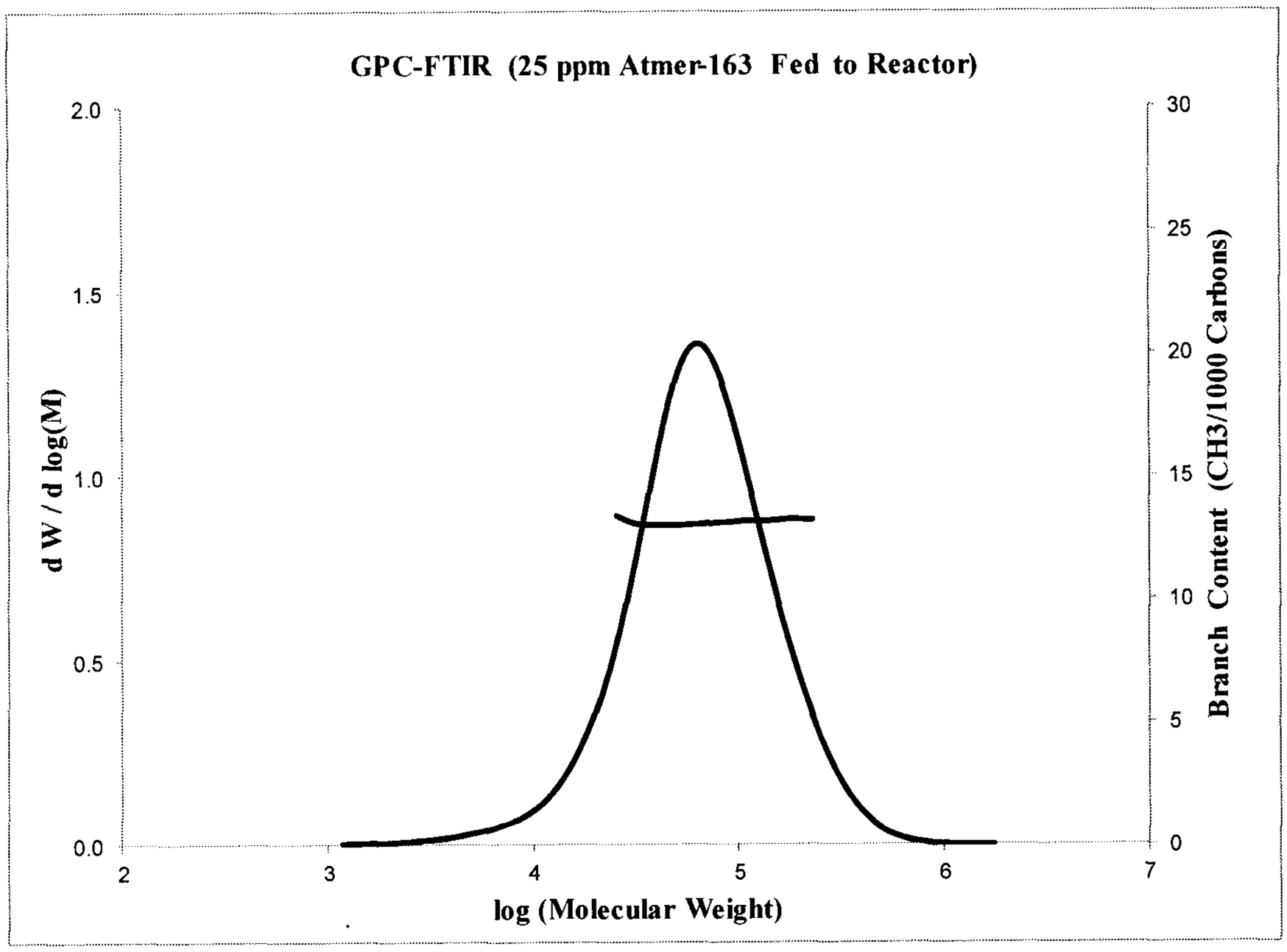


FIGURE 10

