[0004] The composition distribution of an ethylene alpha-olefin copolymer refers to the distribution of comonomer, which form short chain branches, among the molecules that comprise the polyethylene polymer. When the amount of short chain branches varies among the polyethylene molecules, the resin is said to have a "broad" composition distribution. When the amount of comonomer per 1000 carbons is similar among the polyethylene molecules of different chain lengths, the composition distribution is said to be "narrow".

[0005] The composition distribution is known to influence the properties of copolymers, for example, stiffness, toughness, extractable content, environmental stress crack resistance, and heat sealing, among other properties. The composition distribution of a polyolefin may be readily measured by methods known in the art, for example, Temperature Raising Elution Fractionation (TREF) or Crystallization Analysis Fractionation (CRYSTAF).

[0006] It is generally known in the art that a polyolefin's composition distribution is largely dictated by the type of catalyst used and is typically invariable for a given catalyst system. Ziegler-Natta catalysts and chromium based catalysts produce resins with broad composition distributions (BCD), whereas metallocene catalysts normally produce resins with narrow composition distributions (NCD).

[0007] Resins having a broad orthogonal composition distribution (BOCD) in which the comonomer is incorporated predominantly in the high molecular weight chains can lead to improved physical properties, for example toughness properties and environmental stress crack resistance (ESCR). Because of the improved physical properties of resins with orthogonal composition distributions needed for commercially desirable products, there exists a need for controlled techniques for forming polyethylene copolymers having a broad orthogonal composition distribution.

SUMMARY

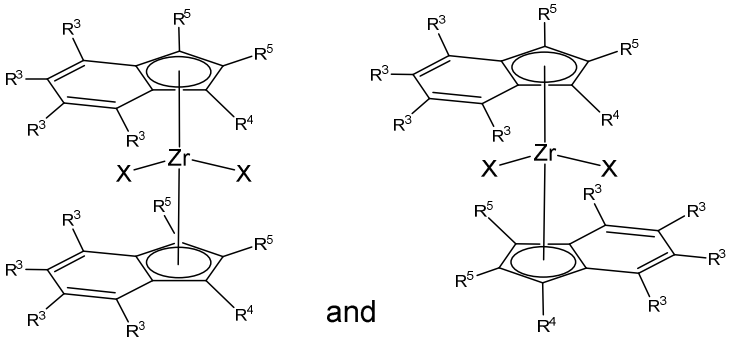
[0008] An example described herein provides a method of alkylating an organometallic compound while substantially normalizing stereochemical configuration. The method includes slurrying the organometallic compound in dimethoxyethane (DME), and adding a solution of RMgBr in DME, wherein R is a methyl group or a benzyl group, and wherein the RMgBr is greater than about 2.3 equivalents relative to the organometallic compound. After the addition of the RMgBr, the slurry is mixed for at least about four hours. An alkylated organometallic is isolated, wherein the methylated species has a meso / rac ratio that is between about 0.9 and about 1.2.

[0009] Another example described herein provides a method of alkylating an organometallic compound while substantially normalizing stereochemical configuration. The method includes slurrying the organometallic compound in ether, and adding a solution of RLi in ether, wherein R is a methyl group or a benzyl group, and wherein the RMgBr is greater than about 2.3 equivalents relative to the organometallic compound. After the addition of the RMgBr, the slurry is mixed for at least about four hours. An alkylated organometallic is isolated, wherein the methylated species has a meso / rac ratio that is between about 0.9 and about 1.2.

[0010] Another example provides a catalyst composition including a first catalyst compound and a second catalyst compound that are co-supported forming a commonly supported catalyst system, wherein the first catalyst compound includes the following formula:

$$(C_5H_aR^1{}_b)(C_5H_cR^2{}_d)HfX_2$$

Each R^1 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. Each R^2 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. The values for a and c are ≥ 3; a+b = c+d = 5. At least one R^1 and at least one R^2 is a hydrocarbyl or substituted hydrocarbyl group. Adjacent groups R^1 and R^2 groups may be coupled to form a ring. Each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group. The second catalyst compound includes a mixture of enantiomers:



MESO RAC ,

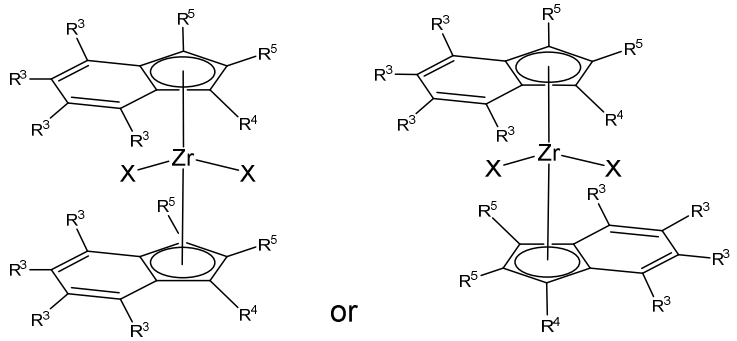
The ratio of the meso enantiomer to the rac enantiomer is substantially normalized during alkylation to between about 1.0 and about 1.2. Each R^3 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. R^4 is a hydrocarbyl group, a

substituted hydrocarbyl group, or a heteoatom group. Each R^5 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. R^3, R^4, and R^5 may be the same or different. Each X is a methyl group.

[0011] Another example provides a method of polymerizing olefins to produce a polyolefin polymer with a multimodal composition distribution, including contacting ethylene and a comonomer with a catalyst system, wherein the catalyst system includes a first catalyst compound and a second catalyst compound that are co-supported to form a commonly supported catalyst system, wherein the first catalyst compound includes the following formula:

$$(C_5H_aR^1{}_b)(C_5H_cR^2{}_d)HfX_2$$

Each R^1 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. Each R^2 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. The values for a and c are ≥ 3; a+b = c+d = 5. At least one R^1 and at least one R^2 is a hydrocarbyl or substituted hydrocarbyl group. Adjacent groups R^1 and R^2 groups may be coupled to form a ring. Each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group. The second catalyst compound includes a mixture of enantiomers:



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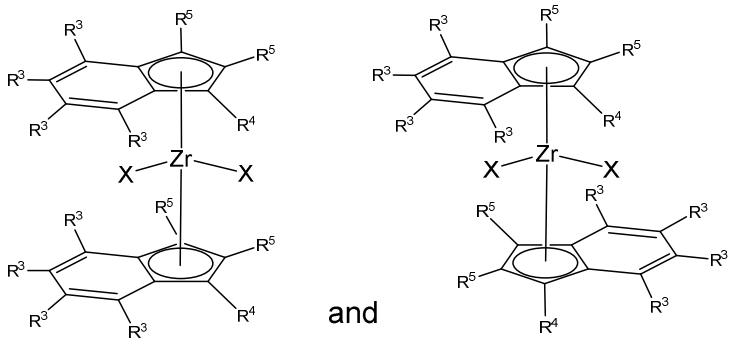
The meso enantiomer is at least about 15 parts in the mixture and the rac enantiomer is less than about 5 parts in the mixture. Each R^3 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. R^4 is a hydrocarbyl group, a substituted hydrocarbyl group, or a heteoatom group. Each R^5 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. R^3, R^4, and R^5 may be the same or different. Each X

is independently a leaving group selected from a labile hydrocarbyl, a substituted hydrocarbyl, a heteroatom group, or a divalent radical that links to an R^3, R^4, or R^5 group.

[0012] Another example provides a polyolefin polymer including ethylene and an alpha-olefin having 4 to 20 carbon atoms, wherein the polefin polymer is formed using a catalyst blend including a first catalyst compound and a second catalyst compound that are co-supported forming a commonly supported catalyst system, wherein the first catalyst compound includes the following formula:

$$(C_5H_aR^1{}_b)(C_5H_cR^2{}_d)HfX_2$$

wherein each R^1 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; each R^2 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; a and c are ≥ 3; a+b = c+d = 5; at least one R^1 and at least one R^2 is a hydrocarbyl or substituted hydrocarbyl group; adjacent groups R^1 and R^2 groups may be coupled to form a ring; and each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group; and the second catalyst compound includes a mixture of enantiomers:



MESO RAC ,

The ratio of one enantiomer to the other enantiomer is at least about 3. Each R^3 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group. R^4 is a hydrocarbyl group, a substituted hydrocarbyl group, or a heteoatom group; each R^5 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; wherein R^3, R^4, and R^5 may be the same or different; and each X is independently a leaving group selected from a labile hydrocarbyl, a substituted hydrocarbyl, a heteroatom group, or a divalent radical that links to an R^3, R^4, or R^5 group.

[0013] Another example provides a method of forming a catalyst composition. The method includes dissolving 1-ethylindenyllithium in dimethoxyethane to form a precursor solution, cooling the precursor solution to about -20 ºC, adding solid $ZrCl_4$ over about five minutes to start a reaction, continuing the reaction overnight, removing volatiles to form a raw product, extracting the raw product with CH_2Cl_2; and removing the CH_2Cl_2 under vacuum to to form a mixture comprising about 19 parts meso-$(1\text{-EtInd})_2ZrCl_2$ and about 1 part rac-$(1\text{-EtInd})_2ZrCl_2$.

[0013a] In one aspect, the present disclosure refers to a method of forming a catalyst composition, comprising: dissolving 1-ethylindenyllithium in dimethoxyethane to form a precursor solution; cooling the precursor solution to about -20 ºC; adding solid $ZrCl_4$ over about five minutes to start a reaction; continuing the reaction overnight; removing volatiles to form a raw product; extracting the raw product with CH_2Cl_2; and removing the CH_2Cl_2 under vacuum to form a mixture comprising about 19 parts meso-$(1\text{-EtInd})_2ZrCl_2$ and about 1 part rac-$(1\text{-EtInd})_2ZrCl_2$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Fig. 1 is a schematic of a gas-phase reactor system, showing the addition of at least two catalysts, at least one of which is added as a trim catalyst.

[0015] Fig. 2 is a plot of a series of polymers that were prepared to test the relative abilities of a series of metallocene catalysts to prepare a resin having about a 1 melt index (MI) and a density (D) of about 0.92.

[0016] Fig. 3 is a plot of the series of polymers of Fig. 2, showing the melt index ratio (MIR) of the series of polymers made by different metallocene (MCN) catalysts.

[0017] Fig. 4 is a flow chart of a method for making a co-supported polymerization catalyst.

DETAILED DESCRIPTION

[0018] It has been discovered that when a support is impregnated with multiple catalysts, new polymeric materials with an improved balance of stiffness, toughness and processibility can be achieved, *e.g.*, by controlling the amounts and types of catalysts present on the support. As described in embodiments herein, an appropriate selection of the catalysts and ratios may be used to adjust the molecular weight distribution (MWD), short chain branch distribution (SCBD), and long-chain branch distribution (LCBD) of the polymer, for example, to provide a polymer with a broad orthogonal composition distribution (BOCD). The MWD, SCBD, and LCBDs would be controlled by combining catalysts with the appropriate weight average

molecular weight (Mw), comonomer incorporation, and long chain branching (LCB) formation under the conditions of the polymerization.

[0019] Employing multiple pre-catalysts that are co-supported on a single support mixed with an activator, such as a silica methylaluminoxane (SMAO), can provide a cost advantage by making the product in one reactor instead of multiple reactors. Further, using a single support also ensures intimate mixing of the polymers and offers improved operability relative to preparing a mixture of polymers of different Mw and density independently from multiple

CLAIMS

What is claimed is:

1. A method of forming a catalyst composition, comprising:

dissolving 1-ethylindenyllithium in dimethoxyethane to form a precursor solution;

cooling the precursor solution to about -20 ºC;

adding solid $ZrCl_4$ over about five minutes to start a reaction;

continuing the reaction overnight;

removing volatiles to form a raw product;

extracting the raw product with CH_2Cl_2; and

removing the CH_2Cl_2 under vacuum to form a mixture comprising about 19 parts meso-$(1\text{-EtInd})_2ZrCl_2$ and about 1 part rac-$(1\text{-EtInd})_2ZrCl_2$.

2. The method of claim 1, comprising:

slurrying the mixture in Et_2O;

adding at least 2.3 equivalents of RMgBr dissolved in ether to the slurry, wherein R is a benzyl group, a methyl group, or a mixture thereof;

drying the slurry;

extracting with warm hexanes; and

filtering to form a catalyst component comprising about 19 parts meso-$(1\text{-EtInd})_2ZrR_2$ and about 1 part rac-$(1\text{-EtInd})_2ZrR_2$.

3. The method of claim 2, comprising:

fluidizing a catalyst support with an inert gas;

heating the support to remove any adsorbed water to form a dried support; and

storing the dried support under an inert gas.

4. The method of claim 3, comprising:

forming a slurry of the dried support in a mixture of toluene and methylaluminoxane; and

drying the mixture to form methyl amluminoxane supported on silica (SMAO).

5. The method of claim 4, comprising:

adding pentane to the SMAO to form a slurry;

dissolving the catalyst component in toluene to form a toluene solution;

adding the toluene solution to the slurry to form a catalyst;

filtering the catalyst from the slurry; and

drying the catalyst.