Title: ACTIVATION FOR OLIGOMERIZATION

Abstract: The oligomerization of ethylene using a chromium catalyst and an aluminoxane activator is well known. The undesired formation of polyethylene as a by-product is also known to occur during prior oligomerization processes. We have discovered that the use of an aluminoxane that is prepared by non-hydrolytic means provides a highly productive activator (co-catalyst) for ethylene oligomerization and mitigates the undesired formation of by-product polyethylene.
ACTIVATION FOR OLIGOMERIZATION

TECHNICAL FIELD

This invention relates to the oligomerization of ethylene using a chromium/diphosphine catalyst and a methylaluminoxane activator.

BACKGROUND ART

Aluminoxanes are commercially available items that are used as activators for olefin polymerization catalysts. Methylaluminoxane (or "MAO") is commonly used because it generally provides high catalyst activity.

MAO can be prepared by the partial hydrolysis of trimethylaluminum ("TMA") using a number of methods that are well known to those skilled in the art. The literature documents several difficulties with the synthesis, storage and transportation of MAO. Most notably, solutions of MAO in hydrocarbon solvents are known to "gel" and/or form solid precipitates after preparation and storage.

Aluminoxanes may also be synthesized via non-hydrolytic processes, as disclosed in U.S. patents 5,777,143 and 5,831,109.

DISCLOSURE OF INVENTION

The present invention provides a process for the oligomerization of ethylene, said process comprising:

1. A process for the oligomerization of ethylene, said process comprising:
   A) a first step wherein an activator is prepared by
      A1) forming an aluminum alkoxide by reacting
          a) an aluminum alkyl selected from the group consisting of
          trimethylaluminum, triethylaluminum and mixtures thereof; with
          b) a source of reactive oxygen selected from the group consisting of
             carbon dioxide; an alcohol; a ketone; a carboxylic acid and mixtures
             thereof; and
      A2) preparing an aluminoxane activator by subjecting said aluminum alkoxide to
          thermolysis; and
   B) a second step comprising contacting:
      a) said activator;
      b) a catalyst comprising a source of chromium and a ligand defined by the
         formula \( (R^1)(R^2)-P^1\)-bridge-\(P^2(R^3)(R^4) \) wherein \( R^1, R^2, R^3 \) and \( R^4 \) are
         independently selected from the group consisting of hydrocarbyl and
heterohydrocarbyl and the bridge is a divalent moiety that is bonded to both phosphorus atoms; and

c) ethylene,

wherein said a), b) and c) are contacted in an oligomerization reactor under oligomerization conditions to prepare a liquid oligomer product.

BEST MODE FOR CARRYING OUT THE INVENTION

PART A CATALYST SYSTEM

The catalyst system used in the process of the present invention must contain three essential components, namely:

(i) a source of chromium:

(ii) a bridged diphosphine ligand; and

(iii) an aluminoxane activator.

Preferred forms of each of these components are discussed below, starting with the activator (iii).

Aluminoxane Activator (iii)

The activator that is used in the process of this invention is characterized by a number of features, including:

a) the aluminoxane activator is prepared from an aluminum alkyl selected from the group consists of trimethyl aluminum (TMA), triethyl aluminum (TEAL) and mixtures thereof;

b) an "aluminum alkoxide" intermediate is prepared by reacting the aluminum alkyl (as above) with a source of reactive oxygen selected from the group consisting of carbon dioxide; an alcohol; a ketone; a carboxylic acid and mixtures thereof; and

c) the aluminum alkoxide intermediate is converted to an aluminoxane by subjecting it to thermolysis.

Each a - c is discussed in more detail below.

Firstly, the aluminum alkyl must be TMA, TEAL, or a mixture of the two. We have observed increased polymer formation when aluminoxanes prepared with other aluminum alkyls are employed. In a preformed embodiment, the aluminoxane is prepared with an aluminum alkyl consisting "essentially of TMA - i.e.: little or no TEAL is used.

Secondly, the aluminum alkyl is reacted with a source of reactive oxygen to prepare an "aluminum alkoxide." Such reactions are well known to those skilled in the art and are widely reported in the literature. The reaction preferably occurs in a solvent (discussed below). The reaction often occurs at room temperature, though heat will
increase to reaction rate. Care should be taken to avoid "run away' explosive reactions especially when using TMA. The use of a tertiary alcohol such as triteriary butyl alcohol or trityl alcohol (as shown in the examples) is especially preferred. The term "aluminum alkoxide" is employed here to describe the reaction product, though it will be recognized by those skilled in the art that the reaction product will often be a mixture of species containing aluminum-oxygen bonds (as opposed to a pure alkoxide).

The aluminum alkoxide is then subjected to a thermolysis reaction i.e.: the aluminum alkoxide is heated. An oligomeric "aluminoxane" is produced by the thermolysis. Preferred conditions for the thermolysis of the above described "alkoxide" (prepared from TMA and a tertiary alcohol) include heating to a temperature of from 80° to 150° C for a period of from 2 to 10 hours.

The preparation of aluminoxane by the thermolysis of an aluminum alkoxide is known and as is described, for example, in U.S. patents 5,777,143 and 5,831,109. One known advantage for this thermolysis route is that it provides the ability to prepare aluminoxanes having very low levels of residual alkyl aluminum (i.e. in contrast, the preparation of aluminoxane by the hydrolysis of TMA with water typically produces a product that contains significant levels of residual TMA. Attempts to lower the level of residual TMA by further hydrolysis generally lead to gels/precipitates).

Aluminoxanes having low levels of residual alkyl are desirable for polymerization reactions. In contrast, we have found that an aluminoxane prepared by thermolysis, but containing comparatively high levels of residual aluminum alkyl, is a very desirable activator for ethylene oligomerization.

Thus, in a preferred embodiment, the amount of oxygen (provided by the reactive oxygen species) is lower - on a molar basis - than the amount of aluminum. It is especially preferred that the oxygen:aluminum molar ratio is from 0.3:1 to 0.8:1.

Preferred solvents for the thermolysis and for the subsequent oligomerization, include \( C_6 \) to \( C_{20} \) aliphatic hydrocarbons; \( C_6 \) to \( C_{20} \) olefins and mixtures thereof. Examples of preferred aliphatic hydrocarbons include hexanes, heptanes and octanes. These hydrocarbons may be linear, branched or cyclic (such as cyclohexane). Examples of \( C_6 \) to \( C_{20} \) olefins include hexenes, heptenes, octenes etc. Likewise, these octenes may be linear or branched and the unsaturation may be at the alpha or an internal position. A mixture of hexene and octene (which may be prepared by the present process) is a particularly preferred non aromatic solvent.
The oligomerization step of the present invention is conducted by contacting the above described activator with a catalyst comprising a source of chromium and a bridged diphosphine ligand and these components are described in further detail below. 

**Chromium Source (“Component (i)”)**

Any source of chromium which allows the oligomerization process of the present invention to proceed may be used. Preferred chromium sources include chromium trichloride; chromium (III) 2-ethylhexanoate; chromium (III) acetylacetonate and chromium carboxyl complexes such as chromium hexacarboxyl.

**Ligand Used in the Oligomerization Process (“Component (ii)”)**

In general, the ligand used in the oligomerization process of this invention is defined by the formula \((R^1)(R^2)-P^1\)-bridge-\(P^2(R^3)(R^4)\) wherein \(R^1, R^2, R^3\) and \(R^4\) are independently selected from the group consisting of hydrocarbyl and heterohydrocarbyl and the bridge is a divalent moiety that is bonded to both phosphorus atoms.

The term hydrocarbyl as used herein is intended to convey its conventional meaning - i.e. a moiety that contains only carbon and hydrogen atoms. The hydrocarbyl moiety may be a straight chain; it may be branched (and it will be recognized by those skilled in the art that branched groups are sometimes referred to as "substituted"); it may be saturated or contain unsaturation and it may be cyclic. Preferred hydrocarbyl groups contain from 1 to 20 carbon atoms. Aromatic groups - especially phenyl groups - are especially preferred. The phenyl may be unsubstituted (i.e. a simple C6H5 moiety) or contain substituents, particularly at an ortho (or "o") position.

Similarly, the term heterohydrocarbyl as used herein is intended to convey its conventional meaning - more particularly, a moiety that contains carbon, hydrogen and heteroatoms (such as O, N, R and S). The heterocarbly groups may be straight chain, branched or cyclic structures. They may be saturated or contain unsaturation. Preferred heterohydrocarbyl groups contain a total of from 2 to 20 carbon + heteroatoms (for clarity, a hypothetical group that contains 2 carbon atoms and one nitrogen atom has a total of 3 carbon + heteroatoms).

It is preferred that each of \(R^1, R^2, R^3\) and \(R^4\) is a phenyl group (with an optional substituent in an ortho position on one or more of the phenyl groups).

Highly preferred ligands are those in which \(R^1\) to \(R^4\) are independently selected from the group consisting of phenyl, o-methylphenyl (i.e. ortho-methylphenyl), o-ethylphenyl, o-isopropylphenyl and o-fluorophenyl. It is especially preferred that none of \(R^1\) to \(R^4\) contains a polar substituent in an ortho position. The resulting ligands are
useful for the selective tetramerization of ethylene to octene-1 with some co product
hexene also being produced. The term "bridge" as used herein with respect to the
ligand refers to a divalent moiety that is bonded to both of the phosphorus atoms in the
ligand - in other words, the "bridge" forms a link between P\(^1\) and P\(^2\). Suitable groups
for the bridge include hydrocarbyl and an inorganic moiety selected from the group
consisting of N(CH\(_3\))-N(CH\(_3\))\(^-\), B(R\(^{6}\))\(^-\), Si(R\(^{6}\))\(_2\)\(^-\), P(R\(^{6}\))\(^-\) or N(R\(^{6}\))\(^-\) where R\(^{6}\) is selected
from the group consisting of hydrogen, hydrocarbyl and halogen.

It is especially preferred that the bridge is -N(R\(^{5}\))- wherein R\(^{5}\) is selected from the
group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy,
substituted aryloxy, halogen, alkoxy carbonyl, carboxyloxy, alkoxy, aminocarbonyl,
carbonylamino, dialkylamino, silyl groups or derivatives thereof and an aryl group
substituted with any of these substituents. A highly preferred bridge is amino isopropyl
(i.e. when R\(^{5}\) is isopropyl).

**PART B PROCESS CONDITIONS**

The chromium (component (i)) and ligand (component (ii)) may be present in any
molar ratio which produces oligomer, preferably between 100:1 and 1:100, and most
preferably from 10:1 to 1:10, particularly 3:1 to 1:3. Generally the amounts of (i) and (ii)
are approximately equal, especially 1:1 and 1:2.

Components (i)-(iii) of the catalyst system utilized in the present invention may
be added together simultaneously or sequentially, in any order, and in the presence or
absence of ethylene in any suitable solvent, so as to give an active catalyst. For
example, components (i), (ii) and (iii) and ethylene may be contacted together
simultaneously, or components (i), (ii) and (iii) may be added together simultaneously or
sequentially in any order and then contacted with ethylene, or components (i) and (ii)
may be added together to form an isolable metal-ligand complex and then added to
component (iii) and contacted with ethylene, or components (i), (ii) and (iii) may be added
together to form an isolable metal-ligand complex and then contacted with
ethylene. The solvent used in the oligomerization is preferably the same non-aromatic
solvent used in the preparation of the activator (especially hexene, octene, or a mixture
of the two).

The catalyst components (i), (ii) and (iii) utilized in the present invention can be
unsupported or supported on a support material, for example, silica, alumina, MgCl\(_2\) or
zirconia, or on a polymer, for example polyethylene, propylene, polystyrene, or
poly(aminostyrene). It is preferred to use the catalyst in unsupported form. If desired
the catalysts can be formed in situ in the presence of the support material or the
support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound.

The oligomerization can be conducted under solution phase, slurry phase, gas phase or bulk phase conditions. Suitable temperatures range from 10°C to +300°C preferably from 10°C to 100°C, especially from 20 to 70°C. Suitable pressures are from atmospheric to 800 atmospheres (gauge) preferably from 5 atmospheres to 100 atmospheres, especially from 10 to 50 atmospheres.

Irrespective of the process conditions employed, the oligomerization is typically carried out under conditions that substantially exclude oxygen, water, and other materials that act as catalyst poisons. Also, oligomerization can be carried out in the presence of additives to control selectivity, enhance activity and reduce the amount of polymer formed in oligomerization processes. Potentially suitable additives include, but are not limited to, hydrogen or a halide source - with the use of hydrogen being especially preferred.

There exist a number of options for the oligomerization reactor including batch, semi-batch, and continuous operation. The reactions of the present invention can be performed under a range of process conditions that are readily apparent to those skilled in the art: as a homogeneous liquid phase reaction in the presence or absence of an inert hydrocarbon diluent such as mixed heptanes; as a two-phase liquid/liquid reaction; as a slurry process where the catalyst is in a form that displays little or no solubility; as a bulk process in which essentially neat reactant and/or product olefins serve as the dominant medium; as a gas-phase process in which at least a portion of the reactant or product olefin(s) are transported to or from a supported form of the catalyst via the gaseous state. Evaporative cooling from one or more monomers or inert volatile liquids is but one method that can be employed to effect the removal of heat from the reaction. The reactions may be performed in the known types of gas-phase reactors, such as circulating bed, vertically or horizontally stirred-bed, fixed-bed, or fluidized-bed reactors, liquid-phase reactors, such as plug-flow, continuously stirred tank, or loop reactors, or combinations thereof. A wide range of methods for effecting product, reactant, and catalyst separation and/or purification are known to those skilled in the art and may be employed: distillation, filtration, liquid-liquid separation, slurry settling, extraction, etc. One or more of these methods may be performed separately from the oligomerization reaction or it may be advantageous to integrate at least some with the reaction; a non-
limiting example of this would be a process employing catalytic (or reactive) distillation. Also advantageous may be a process which includes more than one reactor, a catalyst kill system between reactors or after the final reactor, or an integrated reactor/separater/purifier. While all catalyst components, reactants, inerts, and products could be employed in the present invention on a once-through basis, it is often economically advantageous to recycle one or more of these materials; in the case of the catalyst system, this might require reconstituting one or more of the catalysts components to achieve the active catalyst system. It is within the scope of this invention that an oligomerization product might also serve as a solvent or diluent.

Mixtures of inert diluents or solvents also could be employed. The preferred diluents or solvents are aliphatic and olefinic hydrocarbons and halogenated hydrocarbons such as, for example, isobutane, pentane, heptane, cyclohexane, methylcyclohexane, 1-hexene, 1-octene, chlorobenzene, dichlorobenzene, and the like, and mixtures such as Isopar™.

Techniques for varying the distribution of products from the oligomerization reactions include controlling process conditions (e.g. concentration of components (i)-(iii), reaction temperature, pressure, residence time) and properly selecting the design of the process and are well known to those skilled in the art.

The ethylene feedstock for the oligomerization may be substantially pure or may contain other olefinic impurities and/or ethane. One embodiment of the process of the invention comprises the oligomerization of ethylene-containing waste streams from other chemical processes or a crude ethylene/ethane mixture from a cracker.

In a highly preferred embodiment of the present invention, the oligomerization product produced from this invention is added to a product stream from another alpha olefins manufacturing process for separation into different alpha olefins. As previously discussed, "conventional alpha olefin plants" (wherein the term includes i) those processes which produce alpha olefins by a chain growth process using an aluminum alkyl catalyst, ii) the aforementioned "SHOP" process and iii) the production of olefins from synthesis gas using the so called Lurgi process) have a series of distillation columns to separate the "crude alpha product" (i.e. a mixture of alpha olefins) into alpha olefins (such as butene-1, hexene-1 and octene-1). The mixed oligomer product which is produced in accordance with the present invention is highly suitable for addition/mixing with a crude alpha olefin product from an existing alpha olefin plant (or a "cut" or fraction of the product from such a plant) because the mixed hexene-octene product produced in accordance with the present invention can have very low levels of...
internal olefins. Thus, the oligomer product of the present invention can be readily separated in the existing distillation columns of alpha olefin plants (without causing the large burden on the operation of these distillation columns which would otherwise exist if the present hexene-octene product stream contained large quantities of internal olefins). As used herein, the term "liquid product" is meant to refer to the oligomers produced by the process of the present invention which have from 4 to (about) 20 carbon atoms.

The liquid product from the oligomerization process of the present invention preferably consists of from 20 to 80 weight% octenes (especially from 35 to 75 weight%) octenes and from 15 to 50 weight% (especially from 20 to 40 weight%) hexenes (where all of the weight% are calculated on the basis of the liquid product by 100%. This product may be prepared when using a ligand in which each of R² to R⁴ is a phenyl group having an ortho fluoro substituent and the bridge is a nitrogen atom having an isopropyl substituent (as shown in the examples).

One embodiment of the present invention encompasses the use of components (i) (ii) and (iii) in conjunction with one or more types of olefin polymerization catalyst system (iv) to trimerise ethylene and subsequently incorporate a portion of the trimerisation product(s) into a higher polymer.

Component (iv) may be one or more suitable polymerization catalyst system(s), examples of which include, but are not limited to, conventional Ziegler-Natta catalysts, metallocene catalysts, monocyclopentadienyl or "constrained geometry" catalysts, phosphinimine catalysts, heat activated supported chromium oxide catalysts (e.g. "Phillips"-type catalysts), late transition metal polymerization catalysts (e.g. diimine, diphosphine and salicylaldimine nickelpalladium catalysts, iron and cobalt pyridylidimine catalysts and the like) and other so-called "single site catalysts" (SSC's).

Ziegler-Natta catalysts, in general, consist of two main components. One component is an alkyl or hydride of a Group I to III metal, most commonly Al(Et)₃ or Al(iBu)₃ or Al(Et)₂Cl but also encompassing Grignard reagents, n-butyllithium, or dialkylzinc compounds. The second component is a salt of a Group IV to VIII transition metal, most commonly halides of titanium or vanadium such as TiCl₄, TiCl₃, VCl₄, or VOCl₃. The catalyst components when mixed, usually in a hydrocarbon solvent, may form a homogeneous or heterogeneous product. Such catalysts may be impregnated on a support, if desired, by means known to those skilled in the art and so used in any of the major processes known for co-ordination catalysis of polyolefins such as solution, slurry, and gas-phase. In addition to the two major components described above,
amounts of other compounds (typically electron donors) maybe added to further modify the polymerization behaviour or activity of the catalyst.

Metalocene catalysts, in general, consist of transition metal complexes, most commonly based on Group IV metals, ligated with cyclopentadienyl(Cp)-type groups. A wide range of structures of this type of catalysts is known, including those with substituted, linked and/or heteroatom-containing Cp groups, Cp groups fused to other ring systems and the like. Additional activators, such as boranes or alumoxane, are often used and the catalysts may be supported, if desired.

Monocyclopentadienyl or "constrained geometry" catalysts, in general, consist of a transition metal complexes, most commonly based on Group IV metals, ligated with one cyclopentadienyl(Cp)-type group, often linked to additional donor group. A wide range of structures of this type of catalyst is known, including those with substituted, linked and/or heteroatom-containing Cp groups, Cp groups fused to other ring systems and a range of linked and non-linked additional donor groups such as amides, amines and alkoxides. Additional activators, such as boranes or alumoxane, are often used and the catalysts may be supported, if desired.

A typical heat activated chromium oxide (Phillips) type catalyst employs a combination of a support material to which has first been added a chromium-containing material wherein at least part of the chromium is in the hexavalent state by heating in the presence of molecular oxygen. The support is generally composed of about 80 to 100 wt. % silica, the remainder, if any, being selected from the group consisting of refractory metal oxides, such as aluminium, boria, magnesia, thoria, zirconia, titania and mixtures of two or more of these refractory metal oxides. Supports can also comprise alumina, aluminium phosphate, boron phosphate and mixtures thereof with each other or with silica. The chromium compound is typically added to the support as a chromium (III) compound such as the acetate or acetylacetonate in order to avoid the toxicity of chromium (VI). The raw catalyst is then calcined in air at a temperature between 250 and 1000° C for a period of from a few seconds to several hours. This converts at least part of the chromium to the hexavalent state. Reduction of the Cr (VI) to its active form normally occurs in the polymerization reaction, but can be done at the end of the calcination cycle with CO at about 350° C. Additional compounds, such as fluorine, aluminium and/or titanium may be added to the raw Phillips catalyst to modify it.

Late transition metal and single site catalysts cover a wide range of catalyst structures based on metals across the transition series.
Component (iv) may also comprise one or more polymerization catalysts or catalyst systems together with one or more additional oligomerization catalysts or catalyst systems. Suitable oligomerization catalysts include, but are not limited to, those that dimerise (for example, nickel phosphine dimerisation catalysts) or trimerise olefins or otherwise oligomerize olefins to, for example, a broader distribution of 1-olefins (for example, iron and cobalt pyridyldiimine oligomerization catalysts).

Component (iv) may independently be supported or unsupported. Where components (i) and (ii) and optionally (iii) are supported, (iv) may be co-supported sequentially in any order or simultaneously on the same support or may be on a separate support. For some combinations, the components (i) (iii) may be part or all of component (iv). For example, if component (iv) is a heat activated chromium oxide catalyst then this may be (i), a chromium source and if component (iv) contains an alumoxane activator then this may also be the optional activator (iii).

The components (i), (ii), (iii) and (iv) may be in essentially any molar ratio that produces a polymer product. The precise ratio required depends on the relative reactivity of the components and also on the desired properties of the product or catalyst systems.

An "in series" process could be conducted by first conducting the oligomerization reaction, then passing the oligomerization product to a polymerization reaction. In the case of an "in series" process various purification, analysis and control steps for the oligomeric product could potentially be incorporated between the trimerization and subsequent reaction stages. Recycling between reactors configured in series is also possible. An example of such a process would be the oligomerization of ethylene in a single reactor with a catalyst comprising components (i)-(iii) followed by co-polymerization of the oligomerization product with ethylene in a separate, linked reactor to give branched polyethylene. Another example would be the oligomerization of an ethylene-containing waste stream from a polyethylene process, followed by introduction of the oligomerization product back into the polyethylene process as a co-monomer for the production of branched polyethylene.

An example of an "in situ" process is the production of branched polyethylene catalyzed by components (i)-(iv), added in any order such that the active catalytic species derived from components (i)-(iii) are at some point present in a reactor with component (iv).

Both the "in series and "in situ" approaches can be adaptations of current polymerization technology for the process stages including component (iv). All major
olefin existing polymerization processes, including multiple reactor processes, are considered adaptable to this approach. One adaption is the incorporation of an oligomerization catalyst bed into a recycle loop of a gas phase polymerization process, this could be as a side or recycle stream within the main fluidization recycle loop and or within the degassing recovery and recycle system.

Polymerization conditions when component (iv) is present can be, for example, solution phase, slurry phase, gas phase or bulk phase, with temperatures ranging from -100° C to +300° C and at pressures of atmospheric and above, particularly from 1.5 to 50 atmospheres. Reaction conditions, will typically have a significant impact upon the properties (e.g. density, melt index, yield) of the polymer being made and it is likely that the polymer requirements will dictate many of the reaction variables. Reaction temperature, particularly in processes where it is important to operate below the sintering temperature of the polymer, will typically, and preferably, be primarily selected to optimize the polymerization reaction conditions. Also, polymerization or copolymerization can be carried out in the presence of additives to control polymer or copolymer molecular weights. The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerization process of the present invention.

Slurry phase polymerization conditions or gas phase polymerization conditions are particularly useful for the production of high or low density grades of polyethylene, and polypropylene. In these processes the polymerization conditions can be batch, continuous or semi-continuous. Furthermore, one or more reactors may be used, e.g. from two to five reactors in series. Different reaction conditions, such as different temperatures or hydrogen concentrations may be employed in the different reactors.

Once the polymer product is discharged from the reactor, any associated and absorbed hydrocarbons are substantially removed, or degassed, from the polymer by, for example, pressure let-down or gas purging using fresh or recycled steam, nitrogen or light hydrocarbons (such as ethylene). Recovered gaseous or liquid hydrocarbons may be recycled to a purification system or the polymerization zone.

In the slurry phase polymerization process the polymerization diluent is compatible with the polymer(s) and catalysts, and may be an alkane such as hexane, heptane, isobutane, or a mixture of hydrocarbons or paraffins. The polymerization zone can be, for example, an autoclave or similar reaction vessel, or a continuous liquid full loop reactor, e.g. of the type well-known in the manufacture of polyethylene by the Phillips Process. When the polymerization process of the present invention is carried
out under slurry conditions the polymerization is preferably carried out at a temperature above 0° C, most preferably above 15° C. Under slurry conditions the polymerization temperature is preferably maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerization diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerization within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerization in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

In bulk polymerization processes, liquid monomer such as propylene is used as the polymerization medium.

Methods for operating gas phase polymerization processes are well known in the art. Such methods generally involve agitating (e.g. by stirring, vibrating or fluidizing) a bed of catalyst, or a bed of the target polymer (i.e. polymer having the same or similar physical properties to that which it is desired to make in the polymerization process) containing a catalyst, and feeding thereto a stream of monomer (under conditions such that at least part of the monomer polymerizes in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (e.g. recycled gaseous monomer) and/or volatile liquid (e.g. a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The polymer produced in, and isolated from, gas phase processes forms directly a solid in the polymerization zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerization zone of a gas phase polymerization process the quantity of liquid in the polymerization zone is small in relation to the quantity of polymer present. This is in contrast to "solution phase" processes wherein the polymer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated polymerization zone containing polymerization catalyst, make-up monomer being provided to replace polymerized monomer, and continuously or intermittently withdrawing produced polymer from the polymerization zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being
added to the polymerization zone to replace the catalyst withdrawn from the polymerization zone with the produced polymer.

Methods for operating gas phase fluidized bed processes for making polyethylene, ethylene copolymers and polypropylene are well known in the art. The process can be operated, for example, in a vertical cylindrical reactor equipped with a perforated distribution plate to support the bed and to distribute the incoming fluidizing gas stream through the bed. The fluidizing gas circulating through the bed serves to remove the heat of polymerization from the bed and to supply monomer for polymerization in the bed. Thus the fluidizing gas generally comprises the monomer(s) normally together with some inert gas (e.g. nitrogen or inert hydrocarbons such as methane, ethane, propane, butane, pentane or hexane) and optionally with hydrogen as molecular weight modifier. The hot fluidizing gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentain fine solid particles from the gas stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of polymerization. Catalysts are preferably fed continuously or at regular intervals to the bed. At start up of the process, the bed comprises fluidizable polymer which is preferably similar to the target polymer. Polymer is produced continuously within the bed by the polymerization of the monomer(s).

Preferably means are provided to discharge polymer from the bed continuously or at regular intervals to maintain the fluidized bed at the desired height. The process is generally operated at relatively low pressure, for example, at 10 to 50 atmospheres, and at temperatures for example, between 50 and 135°C. The temperature of the bed is maintained below the sintering temperature of the fluidized polymer to avoid problems of agglomeration.

In the gas phase fluidized bed process for polymerization of olefins the heat evolved by the exothermic polymerization reaction is normally removed from the polymerization zone (i.e. the fluidized bed) by means of the fluidizing gas stream as described above. The hot reactor gas emerging from the top of the bed is led through one or more heat exchangers wherein the gas is cooled. The cooled reactor gas, together with any make-up gas, is then recycled to the base of the bed. In the gas phase fluidized bed polymerization process of the present invention it is desirable to provide additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed under conditions such that the liquid evaporates in the bed thereby absorbing additional heat of polymerization from the bed.
by the "latent heat of evaporation" effect. When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out. In one embodiment of the present invention the volatile liquid is separated from the recycle gas and reintroduced separately into the bed. Thus, for example, the volatile liquid can be separated and sprayed into the bed. In another embodiment of the present invention the volatile liquid is recycled to the bed with the recycle gas. Thus the volatile liquid can be condensed from the fluidizing gas stream emerging from the reactor and can be recycled to the bed with recycle gas, or can be separated from the recycle gas and then returned to the bed.

A number of process options can be envisaged when using the catalysts of the present invention in an integrated process to prepare higher polymers i.e. when component (iv) is present. These options include "in series" processes in which the oligomerization and subsequent polymerization are carried in separate but linked reactors and "in situ" processes in which a both reaction steps are carried out in the same reactor.

In the case of a gas phase "in situ" polymerization process, component (iv) can, for example, be introduced into the polymerization reaction zone in liquid form, for example, as a solution in a substantially inert liquid diluent. Components (i)-(iv) may be independently added to any part of the polymerization reactor simultaneously or sequentially together or separately. Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the polymerization zone. The droplet diameter is preferably within the range 1 to 1000 microns.

Although not usually required, upon completion of polymerization or copolymerization, or when it is desired to terminate polymerization or copolymerization or at least temporarily deactivate the catalyst or catalyst component of this invention, the catalyst can be contacted with water, alcohols, acetone, or other suitable catalyst deactivators a manner known to persons of skill in the art.

A range of polyethylene polymers are considered accessible including high density polyethylene, medium density polyethylene, low density polyethylene, ultra low density polyethylene and elastomeric materials. Particularly important are the polymers having a density in the range of 0.91 to 0.93, grams per cubic centimeter (g/cc) generally referred to in the art as linear low density polyethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown or cast film.

Depending upon the use of the polymer product, minor amounts of additives are typically incorporated into the polymer formulation such as acid scavengers,
antioxidants, stabilizers, and the like. Generally, these additives are incorporated at levels of about 25 to 2000 parts per million by weight (ppm), typically from about 50 to about 1000 ppm, and more typically 400 to 1000 ppm, based on the polymer. In use, polymers or copolymers made according to the invention in the form of a powder are conventionally compounded into pellets. Examples of uses for polymer compositions made according to the invention include use to form fibers, extruded films, tapes, spunbonded webs, molded or thermoformed products, and the like. The polymers may be blown or cast into films, or may be used for making a variety of molded or extruded articles such as pipes, and containers such as bottles or drums. Specific additive packages for each application may be selected as known in the art. Examples of supplemental additives include slip agents, anti-blocks, anti-stats, mould release agents, primary and secondary anti-oxidants, clarifiers, nucleants, uv stabilizers, and the like. Classes of additives are well known in the art and include phosphite antioxidants, hydroxylamine (such as N,N-dialkyl hydroxylamine) and amine oxide (such as dialkyl methyl amine oxide) antioxidants, hindered amine light (uv) stabilizers, phenolic stabilizers, benzofuranone stabilizers, and the like.

Fillers such as silica, glass fibers, talc, and the like, nucleating agents, and colourants also may be added to the polymer compositions as known by the art. The present invention is illustrated in more detail by the following non-limiting examples.

**EXAMPLES**

**Experimental for Impact of TPM-MAO on Catalyst Performance**

**Experimental**

*General experimental conditions*

All air and/or moisture sensitive compounds were handled under nitrogen using standard laboratory techniques or in an inert atmosphere glovebox. Cyclohexane was purified using the system described by Pangborn et al. (Pangborn, A. B. G., M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* 1996, 15, 1518) and then stored over activated molecular sieves. The trimethylaluminum and triphenylmethanol (also known as trityl alcohol) were purchased from Aldrich, and MAO was purchased from Albemarle. They were all used as received.

**Comparative Example 1**

A 600-mL reactor fitted with a stirrer (1700 rpm) was purged 3 times with argon while heated at 80 °C. The reactor was then cooled to 30 °C and a solution made up of
1.46g of a solution of MAO in toluene (10 weight % MAO or 0.146 g MAO), 72.3 g cyclohexane and 6.54g of o-xylene, followed by 48.5 g of cyclohexane were transferred via a stainless steel cannula to the reactor. The MAO was reported to have been made with trimethyl aluminum. We have observed that "modified" MAO (which contains a higher alkyl aluminum, such as tributyl aluminum) increases the level of polyethylene formed. The reactor was then pressurized with ethylene (35 barg) and the temperature adjusted to 45 °C. A cyclohexane solution (14.3 g) of N,N-bis-[di(2-fluorophenyl)phosphine] isopropylamine (4.22 mg, 0.00824 mmol) and chromium acetylacetonate (2.88 mg, 0.00824 mmol) was transferred under ethylene to the pressurized reactor. Immediately after, additional ethylene was added to increase the reactor pressure to 40 barg. The reaction was terminated after 20 minutes by stopping the flow of ethylene to the reactor and cooling the contents to 30 °C, at which point excess ethylene was slowly released from the reactor cooling the contents to 0 °C. The product mixture was transferred to a pre-weighed flask. A sample of the liquid product was analyzed by gas chromatography. The solid products were visible to the eye as small particulates. These solids were collected, weighed and dried at ambient temperature. The mass of product produced was taken as the difference in weights before and after the reactor contents were added to the flask with the ethanol (54.8 g). Batches are shown as "C4's", hexenes as "C6's", and octenes as "C8's" in Table 1.

Inventive Example 2 (Run 1108)

MAO synthesis

In a glovebox, triphenylmethylol 0.725 g, 2.8 mmol) in o-xylene (10 mL) was added to TMA (0.8 mL, 8.3 mmol) in o-xylene (10 mL) in a 50-mL Schlenk flask. The flask was fitted with a condenser. The mixture was then placed in an oil bath at 90 °C and stirred for 24 hours. A clear slightly pale yellow solution resulted. 0.4 mL deuterated THF was added to 0.1 mL aliquot of the reaction mixture in a nuclear magnetic resonance (NMR) tube and analyzed by 1H NMR. This MAO is referred to as MAO type 2 in Table 1.

Inventive Oligomerization experiment 2

A 600-mL reactor fitted with a stirrer (1700 rpm) was purged 3 times with argon while heated at 80 °C. The reactor was then cooled to 30 °C and a solution of MAO prepared above (16.3 g, 0.88 wt% MAO) in 67.4 g cyclohexane, followed by 45.0 g of cyclohexane was transferred via a stainless steel cannula to the reactor. The reactor was then pressurized with ethylene (35 barg) and the temperature adjusted to 46 °C. A
cyclohexane solution (14.3 g) of N,N-bis-[di(2-fluorophenyl)phosphine] isopropylamine (4.22 mg, 0.00824 mmol) and chromium acetylacetonate (2.88 mg, 0.00824 mmol) was transferred under ethylene to the pressurized reactor. Immediately after, additional ethylene was added to increase the reactor pressure to 40 bars (gauge). The reaction was terminated after 20 minutes by stopping the flow of ethylene to the reactor and cooling the contents to 30 °C, at which point excess ethylene was slowly released from the reactor cooling the contents to 0 °C. The product mixture was transferred to a pre-weighed flask. A sample of the liquid product was analyzed by GC-FID. The reaction product was "water clear" with essentially no visible particulate matter (in contrast, the comparative example produced visible particulates). Some solids were collected, weighed and dried at ambient temperature and found to be less than 1% (including catalyst residue). The mass of product produced was taken as the difference in weights before and after the reactor contents were added to the flask with the ethanol (60 g). Results are shown in Table 1.

Inventive Example 3

MAO synthesis (3)
In a glovebox, triphenylmethanol 2.175 g, 8.4) in o-xylene (30 mL) was added to TMA (2.4 mL, 24.9 mmol) in o-xylene (30 mL) in a 100 mL Schlenk flask. The flask was fitted with a condenser. The mixture was then placed in an oil bath at 90 °C and stirred for 24 hours. A clear slightly pale yellow solution resulted. 0.4 mL deuterated THF was added to 0.1 mL aliquot of the reaction mixture in an NMR tube and analyzed by ¹H NMR. This MAO is referred to as MAO 3 in Table 1.

Oligomerization experiment
A 600-mL reactor fitted with a stirrer (1700 rpm) was purged 3 times with argon while heated at 80 °C. The reactor was then cooled to 30 °C and a solution of MAO prepared above (16.3 g, 0.88 wt% MAO) in 65.9 g cyclohexane, followed by 46.5 g of cyclohexane was transferred via a stainless steel cannula to the reactor. The reactor was then pressurized with ethylene (35 barg) and the temperature adjusted to 45 °C. A cyclohexane solution (14.3 g) of N,N-bis-[di(2-fluorophenyl)phosphine] isopropylamine (4.22 mg, 0.00824 mmol) and chromium acetylacetonate (2.88 mg, 0.00824 mmol) was transferred under ethylene to the pressurized reactor. Immediately after, additional ethylene was added to increase the reactor pressure to 40 barg. The reaction was terminated after 20 minutes by stopping the flow of ethylene to the reactor and cooling the contents to 30 °C, at which point excess ethylene was slowly released from the reactor cooling the contents to 0 °C. The product mixture was transferred to a pre-
weighed flask. A sample of the liquid product was analyzed by GC-FID. Again, the product was water clear. Some solids were collected, weighed and dried at ambient temperature. The mass of product produced was taken as the difference in weights before and after the reactor contents were added to the flask with the ethanol (75.9 g).

Results are shown in Table 1. Again, the amount of "residual solids" (polyethylene + catalyst residue) was less than 1 weight %, based on the weight of the liquid oligomer products.
INDUSTRIAL APPLICABILITY

A new activator system for an oligomerization catalyst comprising chromium and a P-N-P ligand is provided. The catalyst/activator system of this invention may be used to prepare an oligomer product that contains hexene-1 and octene-1. The hexene-1 and octene-1 are suitable for the production of a wide variety of end uses, especially as comonomers for the production of ethylene-alpha olefin copolymers.
CLAIMS

1. A process for the oligomerization of ethylene, said process comprising:
   A) a first step wherein an activator is prepared by
      A1) forming an aluminum alkoxide by reacting
          a) an aluminum alkyl selected from the group consisting of
             trimethylaluminum, triethylaluminum and mixtures thereof; with
          b) a source of reactive oxygen selected from the group consisting of
             carbon dioxide; an alcohol; a ketone; a carboxylic acid and mixtures
             thereof; an
   B) a second step comprising contacting:
      a) said activator;
      b) a catalyst comprising a source of chromium and a ligand defined by the
         formula \((R^1)(R^2)-P^1\)-bridge-\(P^2(R^3)(R^4)\) wherein \(R^1, R^2,R^3\) and \(R^4\) are
         independently selected from the group consisting of hydrocarbyl and
         heterohydrocarbyl and the bridge is a divalent moiety that is bonded to both
         phosphorus atoms; and
      c) ethylene,
   wherein said a), b) and c) are contacted in an oligomerization reactor under
   oligomerization conditions to prepare a liquid oligomer product.

2. The process according to claim 1 wherein said source of reactive oxygen is a
   tertiary alcohol selected from the group consisting of tertiary butyl alcohol, trityl alcohol
   and mixtures thereof.

3. The process of claim 1, with the proviso that the molar ratio of oxygen-laluminum
   is from 0.3:1 to 0.8:1 wherein said oxygen is provided by said source of active oxygen
   and said aluminum is provided by said tri aluminum alkyl.

4. The process according to claim 1 wherein said oligomerization is conducted
   under continuous flow conditions.

5. The process according to claim 4 wherein said oligomerization conditions are
   characterized by an operating temperature of from 20 to 70°C and an ethylene
   pressure of from 10 to 50 atmospheres.
6. The process according to claim 1 wherein said chromium and said ligand are provided in a molar ratio of from 1/1 to 1/2.

7. The process according to claim 1 wherein said bridge is defined by the formula 
   - N(R⁵) - and R⁵ is isopropyl.

8. The process according to claim 1 wherein said aluminum alkyl consists essentially of trimethylaluminum.

9. The process according to claim 1 wherein the amount of residual solids is less than 1 weight %, based on the weight of said liquid oligomer products.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC: C07C 2/36 (2006.01), C07C 41/01 (2006.01), C07C 43/13 (2006.01).

According to International Patent Classification (PC) or to both national classification and P C

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C 2/36 (2006.01), C07C 41/01 (2006.01), C07C 43/13 (2006.01).

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
C07C: B01J 31/14

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Total Patent, Canadian Patent Database: aluminim+alkoxide/aliminoxaiie/MAO; ethylene/olefin; oligomer*/trimer*/dimer*; lioii+liydrolty*.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

Date of the actual completion of the international search
29 May 2012 (29.05.2012)

Date of mailing of the international search report
01 June 2012 (01-06-2012)

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Form PCT/ISA/210 (second sheet) (July 2009)
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