

TITLE

POLYMERIZATION OF OLEFINIC ORTHOESTERS

FIELD OF THE INVENTION

Disclosed herein is a method for (co)polymerizing
5 selected olefinic orthoesters using certain late transition
metal containing catalysts. The (co)polymers produced,
which may be hydrolyzed to hydroxyl containing (co)polymers,
and the olefinic orthoester monomers, are novel
compositions.

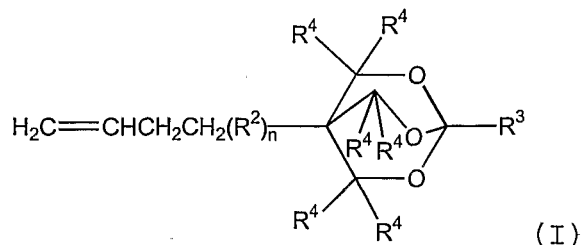
TECHNICAL BACKGROUND

Polyolefins containing functional groups can be made by
a variety of methods, and are important items of commerce,
being used for example for packaging films and molding
resins. Such polymers can be made by free radical and
15 transition metal compound catalyzed processes. Late
transition metal catalysts are especially useful for
including functional groups in olefin polymers, see for
example US5880241, WO98/37110 and WO99/05189 (all of which
are incorporated by reference herein for all purposes as if
20 fully set forth). However, none of these references
describes the polymerization of olefinic orthoesters.
Orthoesters are particularly attractive functional groups
because they may be readily hydrolyzed to hydroxyl groups is
that olefinic bond is on the "alcoholic part" of the
25 original olefinic orthoester, and hydroxyl groups may be
readily reacted to crosslink or otherwise modify the
hydroxyl containing polyolefin. This makes such polymers
useful for example in coatings, and as curable elastomers.

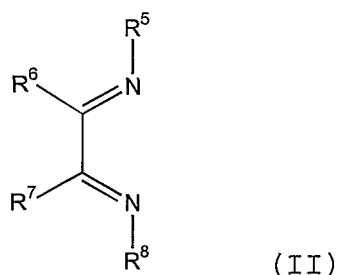
US5116862 and C. J. Palmer, et al., Journal of Labelled
30 Compounds and Pharmaceuticals, vol. 29, p. 829-839 (1991)
(both also incorporated by reference herein for al purposes
as if fully set forth) disclose certain olefinic
orthoesters. None of the orthoesters claimed herein is
specifically disclosed in either of these references.

SUMMARY OF THE INVENTION

This invention concerns a polymerization process, comprising the step of contacting, under polymerizing conditions, an olefin of the formula



and a nickel or palladium complex of a compound of the formula



wherein

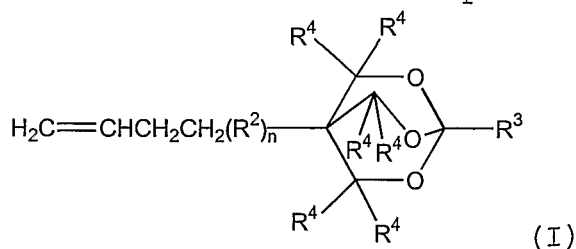
R^2 is alkylene or ether substituted alkylene;
 n is 0 or 1;
 R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl;
 each R^4 is independently hydrogen, a functional group,
 or a hydrocarbyl or substituted hydrocarbyl not containing
 an olefinic or acetylenic group;

R^5 and R^8 are each independently hydrocarbyl or
 substituted hydrocarbyl, provided that the atom bound to the
 imino nitrogen atom has at least two carbon atoms bound to
 it; and

R^6 and R^7 are each independently hydrogen, hydrocarbyl
 or substituted hydrocarbyl, provided that R^6 and R^7 may be
 taken together to form a carbocyclic ring.

Optionally, one or more olefins of the formula $\text{H}_2\text{C}=\text{CHR}^1$,
 wherein R^1 is hydrogen or alkyl, may also be contacted.

This invention also concerns a compound of the formula



wherein:

R^1 is hydrogen or alkyl;

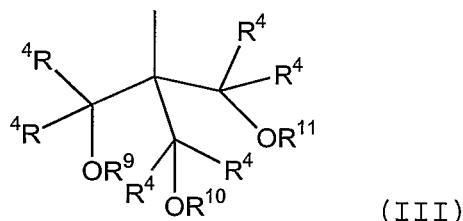
R^2 is saturated hydrocarbylene or ether substituted saturated hydrocarbylene;

n is 0 or 1;

R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl; and

each R^4 is independently hydrogen, a functional group, or a hydrocarbyl or a substituted hydrocarbyl not containing an olefinic or acetylenic group.

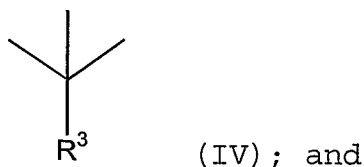
Also disclosed herein is a polyolefin having a side chain of the formula



wherein:

each R^4 is independently hydrogen, a functional group, or a hydrocarbyl or substituted hydrocarbyl not containing an olefinic or acetylenic group;

R^9 , R^{10} and R^{11} are each independently hydrogen or acyl, provided that R^9 , R^{10} and R^{11} taken together may be



R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein, certain terms are used. Some of them are:

A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. As examples of hydrocarbyls may

be mentioned unsubstituted alkyls, cycloalkyls and aryls. If not otherwise stated, it is preferred that hydrocarbyl groups (and alkyl groups) herein contain 1 to about 30 carbon atoms.

5 By "substituted hydrocarbyl" herein is meant a hydrocarbyl group that contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected (e.g., an inert functional group, see below). The substituent groups
10 also do not substantially detrimentally interfere with the oligomerization process or operation of the oligomerization catalyst system. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of
15 "substituted" are rings containing one or more heteroatoms, such as nitrogen, oxygen and/or sulfur. In a substituted hydrocarbyl, all of the hydrogens may be substituted, as in trifluoromethyl.

By "(inert) functional group" herein is meant a group,
20 other than hydrocarbyl or substituted hydrocarbyl, which is inert under the process conditions to which the compound containing the group is subjected. The functional groups also do not substantially deleteriously interfere with any process described herein that the compound in which they are
25 present may take part in. Examples of functional groups include halo (fluoro, chloro, bromo and iodo), and ether such as $-OR^{24}$ wherein R^{24} is hydrocarbyl or substituted hydrocarbyl. In cases in which the functional group may be near a transition metal atom, the functional group alone
30 should not coordinate to the metal atom more strongly than the groups in those compounds that are shown as coordinating to the metal atom, that is they should not displace the desired coordinating group.

By a "cocatalyst" or a "catalyst activator" is meant
35 one or more compounds that react with a transition metal compound to form an activated catalyst species. One such catalyst activator is an "alkyl aluminum compound" which,

herein, is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as, for example, alkoxide, hydride and halogen may also be bound to aluminum atoms in the compound.

5 By "not containing an olefinic or acetylenic group" is meant the compound does not contain a carbon-carbon triple bond or a non-aromatic carbon-carbon double bond.

By "saturated hydrocarbylene" herein is meant a divalent group containing only carbon and hydrogen, and
10 which contains no carbon-carbon multiple (double, triple or aromatic-type) bonds. Typical saturated hydrocarbylene groups are $-(CH_2)_4-$, and $-CH_2CH(CH_2CH_3)CH_2CH_2-$. If not otherwise stated, it is preferred that saturated hydrocarbylene groups herein contain 1 to about 30 carbon
15 atoms.

By "aryl" is meant a monovalent aromatic group in which the free valence is to the carbon atom of an aromatic ring. An aryl may have one or more aromatic rings which may be fused, connected by single bonds or other groups.

20 By "substituted aryl" is meant a monovalent aromatic group substituted as set forth in the above definition of "substituted hydrocarbyl". Similar to an aryl, a substituted aryl may have one or more aromatic rings which may be fused, connected by single bonds or other groups;
25 however, when the substituted aryl has a heteroaromatic ring, the free valence in the substituted aryl group can be to a heteroatom (such as nitrogen) of the heteroaromatic ring instead of a carbon.

By "neutral Lewis base" is meant a compound, which is
30 not an ion, that can act as a Lewis base. Examples of such compounds include ethers, amines, sulfides and organic nitriles.

By "cationic Lewis acid" is meant a cation that can act as a Lewis acid. Examples of such cations are sodium and
35 silver cations.

By "relatively noncoordinating" (or "weakly coordinating") anions are meant those anions as are

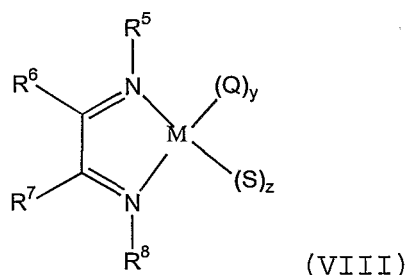
generally referred to in the art in this manner, and the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and

5 S. H. Stares, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by reference. Among such anions are those formed from the aluminum compounds and for example Q^- or S^- (see below), including $R^{23}_3AlS^-$, $R^{23}_2AlClQ^-$, $R^{23}AlCl_2Q^-$, and " $R^{23}AlOQ^-$ ", wherein R^{23} is alkyl. Other useful
10 noncoordinating anions include BAF^- {BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, SbF_6^- , PF_6^- , and BF_4^- , trifluoromethanesulfonate, p-toluenesulfonate, $(R_fSO_2)_2N^-$, and $(C_6F_5)_4B^-$.

The transition metal complexes used in the process
15 disclosed herein contain α -diimine ligands. Such transition metal complexes are known to polymerize various olefins (but not known to polymerize orthoesters) under various conditions. The structures of such complexes, how to prepare them, how to prepare active polymerization catalysts
20 from them (if they are not already active polymerization catalysts), and polymerization conditions are known in the art, see for example US5880241, US5866663, US5852145, WO99/05189, WO97/48739, WO98/49208, WO98/37710, WO98/03167, WO97/48737 and WO97/38024, all of which are hereby
25 incorporated by reference herein for all purposes as if fully set forth. These references, especially US5880241, describe preferred structures for the α -diimines and their complexes, and these are also preferred herein. In such complexes herein it is preferred that the transition metal
30 is nickel. The α -diimine complex may be added directly to the polymerization as a compound which will directly catalyze polymerization (see Example 3), may be added a complex that is chemically modified (e.g., with a co-catalyst) to form an active polymerization catalyst (see
35 example 4), or ingredients to form the complex in situ may added to the process.

The above references on α -diimine complexes also contain information on various types of polymerization processes (gas phase, solution, slurry, continuous, batch and semi-batch), and conditions and preferred conditions for running such processes. When applicable (for example it is unlikely that gas phase polymerization will result in much incorporation of most orthoester monomers since these monomers are not very volatile), such conditions and preferred conditions are applicable herein.

For instance one method of running the polymerization is to use a complex of the formula



wherein R^5 , R^6 , R^7 and R^8 are as defined above, M is Ni or Pd, Q and S are each anions, and y and z are integers so that $y+z=m$, wherein m is the oxidation state of M. Preferably m is 2. This complex is typically contacted with the olefinic orthoester(s), optionally with one or more other olefinic monomer(s), at a temperature of about -100°C to about $+200^\circ\text{C}$, preferably 0°C to 100°C , and also with a first compound W, which is a neutral Lewis acid capable of abstracting either Q^- or S^- from (VIII) to form WQ^- or WS^- , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion, to form an active polymerization catalyst. If none of Q^- or S^- are alkyl, hydride or acyl, either W or a second compound is added that is capable of reacting with (VIII) to remove a Q^- or S^- and replace it with a hydride, alkyl or acyl anion. Typically W is chosen to be able to do this also, if needed. A typical and preferred W is an alkylaluminum compound, which is not only capable of abstract Q^- or S^- , but will also provide an alkyl group if needed. Useful alkylaluminum compounds include aluminoxanes such as methyl aluminoxane, and alkyl aluminum chlorides

such as diethylaluminum chloride, ethylaluminum dichloride and ethylaluminum sesquichloride. Q^- and S^- may be different or the same. Preferred Q and S are halide, especially chloride and bromide, and carboxylate, and chloride and bromide are especially preferred. See Example 4 for such a polymerization.

Any nickel or palladium complex of a bidentate ligand which is capable of (co)polymerizing olefins containing polar groups such as esters, may also be used in the copolymerization herein. Such complexes may be found in US5866663, US5714556, WO98/30610, WO98/30609, WO98/47934 and WO99/05189, WO00/06620 and U.S. Patent Application 09/539560 (filed 31 March 2000), all of which are hereby incorporated by reference herein for all purposes as if fully set forth.

It is preferred in all processes another olefin is present, and that R^1 is hydrogen or n-alkyl containing 1 to 18 carbon atoms, especially preferably R^1 is hydrogen or methyl, and more preferably R^1 is hydrogen (the olefin is ethylene).

Compounds of the formula (I) can be prepared by the methods as set forth in the Examples (see Examples 1 and 2). Variations in the starting components (and process conditions required to utilize those starting components) will be recognized, or can be determined without undue experimentation, by those of ordinary skill in the art as required to achieve the desired end compound.

In (I) it is preferred that:

n is 1; and/or

R^2 is alkylene, more preferably that R^2 is $-(CH_2)_m-$

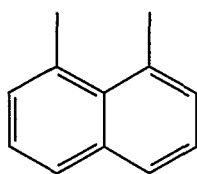
wherein m is 1 to 18; and/or

each R^4 is hydrogen; and/or

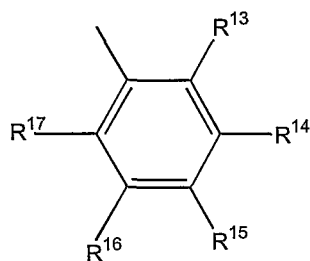
R^3 is hydrocarbyl, more preferably alkyl, and especially preferably methyl.

In (II) it is preferred that:

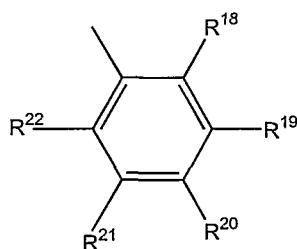
R^6 and R^7 are hydrogen, methyl, or taken together are



; and/or

 R^5 is

(V)

and R^8 is

(VI)

wherein

R^{13} and R^{18} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group,

R^{14} , R^{15} , R^{16} , R^{19} , R^{20} and R^{21} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, and

R^{17} and R^{22} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, and provided that any two of R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} and R^{22} that are vicinal to one another, taken together may form a ring.

In (III) it is preferred that:

R^9 , R^{10} and R^{11} are all hydrogen; or

R^9 and R^{10} are hydrogen and R^{11} is acyl; and/or

acyl is $R^{25}C(O)-$ wherein R^{25} is hydrocarbyl or substituted hydrocarbyl, more preferably hydrocarbyl, especially preferably alkyl, and very preferably methyl.

(III) is a pendant group, and in (III) the bond not labeled is a free bond. By a pendant group is meant that

(III) is connected to the main polymer chain either directly

by the free bond, or being connected through an intermediate divalent groups such as $-\text{CH}_2\text{CH}_2\text{R}^2-$. However since "chain walking" may take place during some of these polymerizations (see previously incorporated US5880241), these connecting groups may vary.

In structure (IV) the 3 bonds which have no groups at the ends are free covalent bonds, not methyl groups.

Polyolefins in which (III) is present in the ester or orthoester form may be hydrolyzed by standard methods for hydrolyzing these functional groups, such as reaction with water and/or alcohols. These hydrolyses are usually acid and/or base catalyzed reactions.

Polyolefins which contain (III) in which at least one of R^9 , R^{10} , or R^{11} is hydrogen may be crosslinked by any reaction known to crosslink hydroxyl containing polymers may be used. For instance, the polymer may be reacted with di- or higher functional epoxides, isocyanates, carboxylic acids, acyl halides, esters, carboxylic anhydrides and organic carbonates. These crosslinking compounds may be monomeric (of low molecular weight) or polymeric. If the polyolefin containing (III) happens to be elastomeric, a crosslinked elastomer results. These elastomers may be particularly useful as sealants and caulks. Various methods are known in the art for delaying such crosslinking reactions, such as masking the one of the groups taking place in the crosslinking reaction and "activating" by heating.

In the Examples, the following abbreviations are used:

DSC - Differential Scanning Calorimetry

PMAO-IP - poly(methylaluminoxane) (Akzo-Nobel Inc.)

RB - round-bottomed

RT - room temperature

TCE - 1,1,2,2-tetrachloroethane

THF - tetrahydrofuran

Melting points of polymers are taken as the peak of the melting endotherm.

Example 1Preparation of 2,2-Bis(hydroxymethyl)-10-undecen-1-ol

In a 300 mL RB flask equipped with a stirrer and reflux condenser were added undecylenic aldehyde (10-undecenal) (20.98 g) and 37% formaldehyde (83.24 g). To this solution a 50% solution of sodium hydroxide (10.41 g) was added at such a rate so that the temperature remained below 50°C. After the addition, the solution was heated at 90°C for one h. The solution was allowed to cooled to RT and then neutralized with formic acid. The solution was then concentrated at reduced pressure, then chloroform (250 mL) added. The resulting mixture was filtered through Celite® and the filtrate concentrated at reduced pressure and then vacuum distilled. The fraction boiling at 142-151°C at ~200 Pa (absolute) was collected (13.99 g, 48.66% yield).

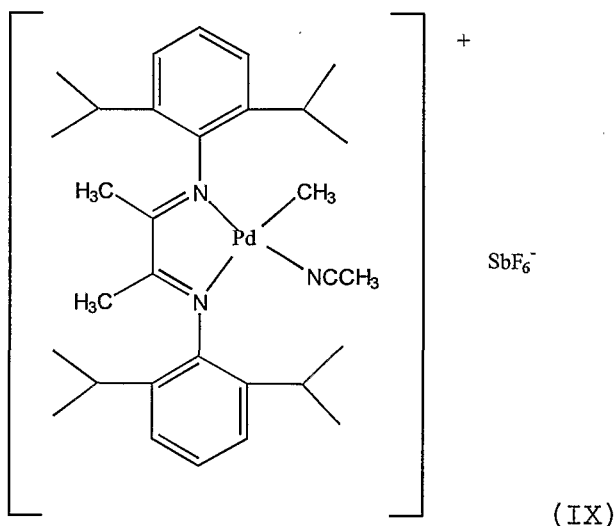
Example 2Preparation of 1-Methyl-4-(8-nonenyl)-2,6,7-trioxabicyclo[2.2.2]octane (VII)

In a oven dried 250 mL RB flask equipped with a stirrer, thermometer and a distillation head were add 2,2-bis-(hydroxymethyl)-10-undecen-1-ol (38.0 g), triethyl orthoacetate (28.4 g), dioctyl phthalate (132.2 g) and 4-ethylbenzene sulfonic acid (0.132 g). The resulting mixture was placed under nitrogen and heated to 140°C during which the theoretical amount of ethanol was distilled off. The reaction was allowed to cool and then placed under vacuum. When a vacuum of less than 133 Pa was achieved the reaction was heated to a maximum temperature of 220°C during which the desired product distilled off as a clear liquid (39.05 g, 93.06% yield). This was then redistilled, ¹H NMR (CDCl₃) : 5.75 (m, 1H), 4.9 (m, 2H), 3.85 (s, 6H), 2.00 (m, 2H), 1.30 (s, 3H), 1.4-1.0 (m, 12H).

Example 3Synthesis of an Ethylene Copolymer of CH₂=CH(CH₂)₇C(CH₂O)₃CCH₃Using a Pd Catalyst

In a drybox, (IX) (0.0848 g, 0.1 mmol), and CH₂=CH(CH₂)₇C(CH₂O)₃CCH₃ [(VII), 5.0 g, 0.0294 mole] were

dissolved in 40 mL CH_2Cl_2 in a 200 mL Schlenk flask. This was brought out of the drybox and was purged with 1 atm ethylene for 15 min. The solution was then stirred under 1 atm of ethylene for 48 hr at RT. The mixture was then
 5 poured into a 500 mL beaker and was added 300 mL methanol. The polymer was isolated and was redissolved in 50 mL CH_2Cl_2 . To this was added 300 mL methanol. The isolated polymer was dried overnight in vacuo at 50°C . A viscous oil (13.5 g) was obtained. Based on ^1H NMR(CD_2Cl_2), the orthoester
 10 incorporation was 2.8 mole % $\{\delta$ 3.88 (s, 6H, $-\text{CH}_2\text{-O-}$); $-\text{CMe-}$ resonances overlapped with that of the methyls (0.8-1.0) on the copolymers, the methylene peaks overlapped with that of the copolymers (1.1-1.4). The polymer was branched based on ^1H NMR (91 Me/1000 CH_2). Gel permeation chromatography (THF, polystyrene standard): $M_w = 186,485$; $M_n = 61,384$; $M_w/M_n =$
 15 3.0.



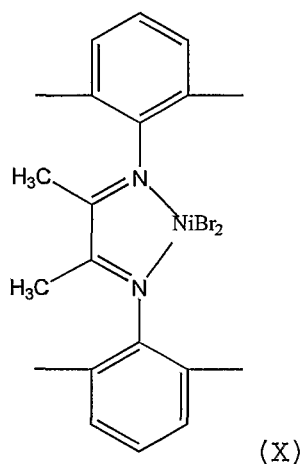
Example 4

Synthesis of an Ethylene Copolymer of $\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{C}(\text{CH}_2\text{O})_3\text{CCH}_3$

Using a Ni catalyst

20 In a drybox, (X) (8.7 mg, 0.017 mmol), $\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{C}(\text{CH}_2\text{O})_3\text{CCH}_3$ [(VII), 5.0 g], and 35 mL toluene were mixed in a 200 mL Schlenk flask. The mixture was brought out of the drybox and was placed under 1 atm of
 25 ethylene. The mixture was purged with ethylene while cooled in an ice-water bath for 15 min. PMAO-IP (1.2 mL, 13.5 wt% toluene solution) was injected into the reaction mixture and

this was allowed to stir for 3 h at 0°C under 1 atm of ethylene. To the mixture was slowly added 100 mL methanol. The mixture was allowed to stir at RT for 30 min. White solid copolymer was filtered, washed with 6X20 mL methanol and dried in full vacuo at 100°C overnight. White polymer (6.15 g) was obtained. Both ^1H NMR and ^{13}C NMR showed that comonomer was incorporated, but was likely in the alcohol form since there were no orthoester or ester groups in the polymer. ^1H NMR(TCE- d_2 , 120°C): δ 3.52 (d, 6H, $-\text{CH}_2\text{-OH}$), 1.2-1.4 (s, $-\text{CH}_2\text{-}$ of the polymer), 0.8-1.0 (m, $-\text{CH}_3$ of the polymer). The comonomer incorporation was 0.6 mole %. The polymer had 5Me/1000CH₂. DSC(10°C/min, 2nd heat): m.p. = 121°C (94.6 J/g).



Example 5

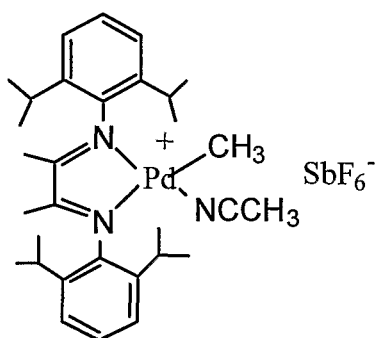
Hydrolysis of Polymer

The poly(olefin-orthoester) made in Example 3 (1.0 g) was dissolved in THF (10 mL) then 0.20 mL of a 0.242 M solution of p-toluenesulfonic acid added. Aliquots were withdrawn after 2 and 4 h and the solvent removed from each aliquot under vacuum. ¹H NMR showed the complete hydrolysis of the orthoester after 2 h. After stirring overnight, the THF was removed from the main portion of the reaction under vacuum and chloroform added. The resulting solution was washed with 5% sodium carbonate (2 x 10 mL) and then with water. The organic phase was dried over sodium sulfate, filtered, concentrated and then dried under vacuum affording 0.55 g of the polyol. IR showed two carbonyl resonances at 1744 and 1722 cm⁻¹, indicating partial hydrolysis of the

orthoester and/or carboxylic ester groups (which result from hydrolysis of the orthoester).

Comparative Example A

In a drybox, (IX) (0.0848 g, 0.1 mmol), and
 5 $\text{CH}_2=\text{CHCH}_2\text{C}(\text{CH}_2\text{O})_3\text{CCH}_3$ (5.0 g, 0.0294 mole), were dissolved in
 40 mL CH_2Cl_2 in a 200 mL Schlenk flask. This was brought out
 of the drybox and was purged with 1 atm ethylene for 15 min.
 The solution was then stirred under 1 atm of ethylene for 48
 hr at RT. The mixture was then poured into a 500 mL beaker
 10 and 300 mL methanol was added. The polymer was isolated and
 was redissolved in 50 mL CH_2Cl_2 . To this was added 300 mL
 methanol. The isolated polymer was dried overnight in vacuo
 at 50°C. Viscous oil (22 g) was obtained. Based on ^1H
 NMR(CD_2Cl_2), no orthoester monomer was incorporated. The
 15 polymer was polyethylene. Gel permeation chromatography
 (THF, polystyrene standard): $M_w = 59,536$; $M_n = 33,872$;
 $M_w/M_n = 1.8$.

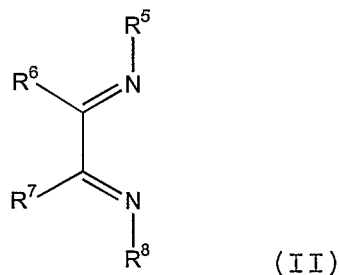


Pd Catalyst Used in the Reaction

CLAIMS

What is claimed is:

1. A polymerization process comprising the step of contacting, under polymerizing conditions, one or more
 5 olefins and a nickel or palladium complex of a compound of the formula

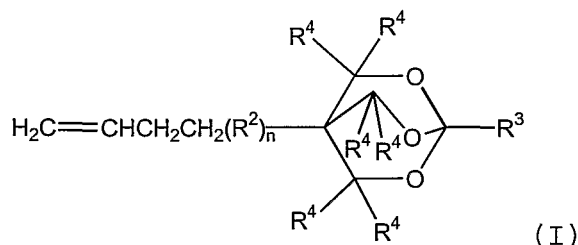


wherein

10 R^5 and R^8 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

R^6 and R^7 are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^6 and R^7 may be
 15 taken together to form a carbocyclic ring,

characterized in that an olefin is of the formula



wherein

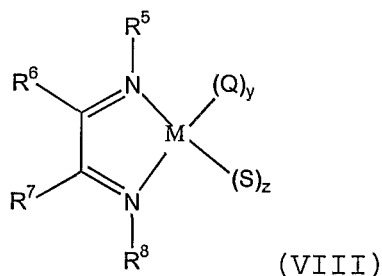
R^2 is alkylene or ether substituted alkylene;

20 n is 0 or 1;

R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^4 is independently hydrogen, a functional group, or a hydrocarbyl or substituted hydrocarbyl not containing an olefinic or acetylenic group.

2. The process as recited in claim 1, characterized in that said complex is



wherein:

M is Ni or Pd;

Q and S are each independently anions; and

y and z are integers so that $y+z=m$, wherein m is the oxidation state of M;

and wherein said complex is contacted with a first compound W, which is a neutral Lewis acid capable of abstracting either Q^- or S^- to form WQ^- or WS^- , provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion, to form an active polymerization catalyst, provided that if none of Q^- or S^- are alkyl, hydride or acyl, either W or a second compound is added which is capable of reacting with said complex to remove a Q^- or S^- and replace it with a hydride, alkyl or acyl anion.

3. The process as recited in claim 2, characterized in that W is an alkylaluminum compound.

4. The process as recited in claim 1, characterized in that said temperature is about 0°C to about 100°C.

5. The process as recited in claim 1, characterized in that:

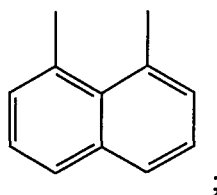
n is 1;

R^2 is $-(CH_2)_m-$ wherein m is 1 to 18; and/or

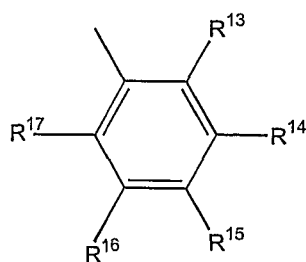
each R^4 is hydrogen;

R^3 is hydrocarbyl;

R^6 and R^7 are hydrogen, methyl, or taken together are

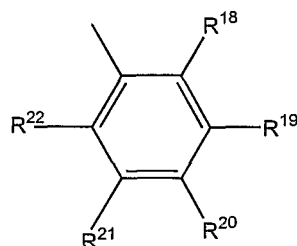


R⁵ is



(V); and

R⁸ is



(VI)

5 wherein:

R¹³ and R¹⁸ are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group;

10 R¹⁴, R¹⁵, R¹⁶, R¹⁹, R²⁰ and R²¹ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group; and

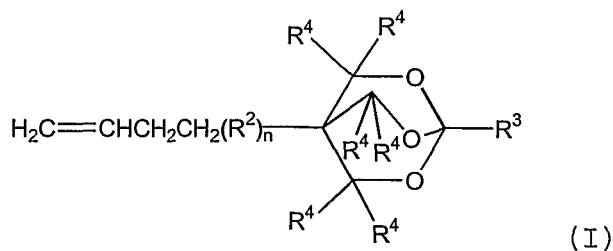
R¹⁷ and R²² are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

15 and provided that any two of R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹ and R²² that are vicinal to one another, taken together may form a ring.

6. The process as recited in any one of claims 1-5, characterized in that at least one olefin of the formula H₂C=CHR¹ is present, wherein R¹ is hydrogen or alkyl.

7. The process as recited in claim 6, characterized in that R¹ is hydrogen.

8. A compound of the formula



(I)

wherein:

R^2 is saturated hydrocarbylene or ether substituted saturated hydrocarbylene;

n is 0 or 1;

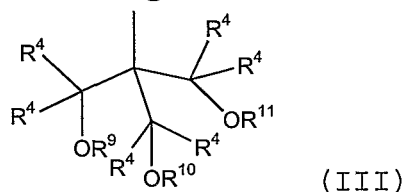
R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl; and

each R^4 is independently hydrogen a functional group, or hydrocarbyl or substituted hydrocarbyl not containing an olefinic or acetylenic group.

9. The compound as recited in claim 8, characterized in that n is 1; R^2 is alkylene; each R^4 is hydrogen; and R^3 is hydrocarbyl.

10. The compound as recited in claim 9, characterized in that R^2 is $-(CH_2)_m-$ wherein m is 1 to 18; and R^3 is alkyl.

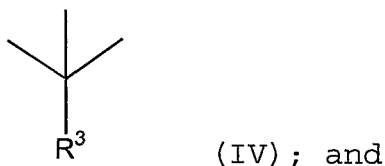
11. A polyolefin having a side chain of the formula



wherein:

each R^4 is independently hydrogen, a functional group, or a hydrocarbyl or substituted hydrocarbyl not containing an olefinic or acetylenic group;

R^9 , R^{10} and R^{11} are each independently hydrogen or acyl, or R^9 , R^{10} and R^{11} taken together are



R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl.

12. The polyolefin as recited in claim 12, characterized in that each R^4 is hydrogen.

13. The polyolefin as recited in claim 11 or 12, characterized in that each R^3 is hydrogen.

14. The polyolefin as recited in claim 11 or 12 which has been crosslinked.